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Role of the breathing mode in a strongly coupled $E \otimes \varepsilon$ Jahn–Teller system

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Abstract. The theoretical absorption spectrum of a vibronic $E \otimes \varepsilon$ system exhibits two main peaks of different height and width, and, at very strong Jahn–Teller energy, other peaks at higher energies (cone resonances or Slonczewski resonances). Tetrameric cations of the group V elements (P_4^+ , As_4^+ , Sb_4^+) can be pictured as strongly coupled $E \otimes \varepsilon$ Jahn–Teller systems; however, high resolution photoelectron spectra available in the literature exhibit only two broad spectral bands. To explain the disappearance of the cone resonances, we have considered a two-mode vibronic model, that, besides a strong linear interaction with the mode ε , also includes a linear interaction with the total symmetric mode α_1 (breathing mode); we have also considered separately off-diagonal second-order effects on the $E \otimes \varepsilon$ Jahn–Teller system. The analysis has been carried out in the framework of the recursion Lanczos technique, properly implemented. We have verified that the Slonczewski resonances are quenched by the breathing mode, even in the case of moderate coupling; we have then compared our $E \otimes (\varepsilon + \alpha_1)$ model with the available experimental spectra of group V tetrameric clusters.

1. Introduction

The vibronic $E \otimes \varepsilon$ system, a double degenerate electronic state of symmetry E interacting with a two-dimensional harmonic oscillator of symmetry ε , is one of the most studied Jahn–Teller systems [1–10]: besides its intrinsic interest, the $E \otimes \varepsilon$ system is the prototype of other more complicated vibronic systems, and has thus become an enticing model on which to test new theoretical treatments.

Among the various procedures, the iterative technique based on the Lanczos–Haydock–Heine–Kelly recursion method [11, 12] has turned out to be particularly efficient, because the coefficients of the recursion, for this vibronic system, have been obtained in analytic form [13]. Then it is possible to study the system (from the point of view of the optical properties) in the very strong vibronic coupling regime, giving theoretical evidence for the cone resonances or Slonczewski resonances [14].

From the experimental point of view, the simplest systems, where the twofold degenerate E electronic states exhibit a strong Jahn–Teller coupling with a two-dimensional mode ε , are the tetrameric cations of the group V elements (P_4^+ , As_4^+ , Sb_4^+). The high resolution photoelectron spectra [15] of the $(1e)^{-1}$ band present two broad peaks and no cone resonances. The main mechanism of vibronic interaction suggested in previous papers [15, 16] to explain the $(1e)^{-1}$ band shape of the experimental photoelectron spectra has been a quadratic $E \otimes \varepsilon$ Jahn–Teller model [7]. The effect of the breathing mode, due to

the diagonal form of the corresponding interacting Hamiltonian [17], has been taken into account convoluting with a Poisson distribution the spectrum calculated in the quadratic $E \otimes \varepsilon$ Jahn–Teller model [16]. However, what the leading mechanism is that washes out cone resonances has not yet clearly emerged. In this paper we analyse *separately* the effect of the breathing mode (or equivalently the effect of a Poisson shape convolution) on the strongly coupled $E \otimes \varepsilon$ model, taking advantage of the commuting properties [17] of the matrices describing the linear coupling to the mode ε and α_1 . After analysing the effect of the off-diagonal second-order term, we show that the role of the total symmetric mode is more important than usually believed. The calculations of the convolution with a Poisson distribution function are made in the framework of the Lanczos technique (section 2), appropriately implemented to avoid some usual numerical inaccuracies. In section 3 the results obtained are compared with the $(1e)^{-1}$ band of the tetrameric cations P_4^+ , As_4^+ and Sb_4^+ and the effect of the off-diagonal second-order term is also shown. Section 4 contains the conclusions.

2. Model and calculation procedure

High resolution experimental photoelectron spectra [15] of the tetrameric cations P_4^+ , As_4^+ and Sb_4^+ exhibit, besides the $(1e)^{-1}$ band with two broad peaks, a $(2a)^{-1}$ single band (according to the Franck–Condon picture) corresponding to the transition from the non-degenerate ground state to the non-degenerate 2A_1 state. For the $(2a)^{-1}$ single band, discrete vibrational structure is well resolved in P_4^+ and As_4^+ cases, less well in the Sb_4^+ case; in all tetramers, it is evident that the α_1 mode is excited and that the discrete structure with Poisson profile is a consequence of the coupling of the electrons with the nuclear totally symmetric vibrations. So it becomes natural to assume for the $(1e)^{-1}$ band a two-phonon vibronic model where a double degenerate electronic state of symmetry E interacts both with the two-dimensional mode (ε mode) and with the totally symmetric mode (α_1 mode).

Let us indicate with ϕ_1 and ϕ_2 the degenerate electronic states of symmetry E for the nuclei fixed in the symmetry position. We take the energy of the electron state as the reference energy and we consider a linear coupling with the modes ε and α_1 . The electron–phonon coupling Hamiltonian has the following well known form:

$$H_{e-p} = k_\varepsilon \hbar \omega_\varepsilon \begin{vmatrix} -q_1 & q_2 \\ q_2 & q_1 \end{vmatrix} + k_{\alpha_1} \hbar \omega_{\alpha_1} \begin{vmatrix} q_3 & 0 \\ 0 & q_3 \end{vmatrix}. \quad (1)$$

In equation (1) q_1 , q_2 and q_3 are dimensionless normal coordinates related to the normal symmetrized coordinates Q_1 , Q_2 (mode ε) and Q_3 (mode α_1) in the form $q = Q\sqrt{M\omega/\hbar}$; $\hbar\omega_\varepsilon$ and $\hbar\omega_{\alpha_1}$ are the energies of the modes ε and α_1 ; k_ε and k_{α_1} are dimensionless coupling constants related to the Huang–Rhys factor S in the form $2S_\varepsilon = k_\varepsilon^2$; $2S_{\alpha_1} = k_{\alpha_1}^2$; S is the Jahn–Teller energy E_{JT} in units of the phonon energy, i.e. $S\hbar\omega = E_{JT}$.

We denote by H_L the diagonal second-order terms for each mode, i.e.

$$H_L = \frac{1}{2}\hbar\omega_\varepsilon (q_1^2 + q_2^2) + \frac{1}{2}\hbar\omega_{\alpha_1} q_3^2. \quad (2a)$$

The Jahn–Teller Hamiltonian of the $E \otimes (\varepsilon + \alpha_1)$ system

$$H_{JT} + H_L + H_{e-p}$$

can be written as the sum of the Jahn–Teller Hamiltonian for the $E \otimes \varepsilon$ system and for the $E \otimes \alpha_1$ system, and can be expressed as

$$H_{JT} = H_{JT,\varepsilon} + H_{JT,\alpha_1} \quad (2b)$$

where $H_{JT,\varepsilon}$ and H_{JT,α_1} commute with each other [17]. Furthermore from the point of view of the optical properties, concerning the transition from the ground state to the double degenerate state, $H_{JT,\varepsilon}$ leads to the typical linear $E \otimes \varepsilon$ spectral distribution exhibiting two peaks separated by almost $2\sqrt{S\hbar\omega_\varepsilon}$, and for very large S , a sequence of other peaks of decreasing amplitude, due to the resonance between the vibrational levels of the two adiabatic surfaces (the Slonczewski resonances or cone resonances [14]). The Hamiltonian term H_{JT,α_1} corresponds to a two-dimensional shifted harmonic oscillator and leads to the well known Poisson spectral distribution function. So we can regard the $E \otimes (\varepsilon + \alpha_1)$ system also as a Jahn–Teller system ‘convoluted’ with a Poisson distribution function. This convolution can be performed in the framework of the Lanczos technique [18] and presents here the advantage of requiring less memory storage than the direct treatment of the $E \otimes (\varepsilon + \alpha_1)$ system; furthermore it allows us to obtain very accurate results on properly choosing the basis functions and the initial state in the construction of the Lanczos chain.

It is convenient to briefly summarize the general concepts [11, 12] and methodology of the Lanczos recursion method. Let us indicate with $\{\phi_i\}$ ($i = 1, 2, \dots, N$) a complete set of basis functions, for the representation of the operator H . Starting from a seed state $|f_0\rangle$, given by whatever chosen linear combination of the $\{\phi_i\}$, we can generate a hierarchical chain of orthonormal states $|f_0\rangle, |f_1\rangle, \dots, |f_N\rangle$ by means of successive applications of the operator H as follows:

$$|F_1\rangle = (H - a_0)|f_0\rangle \quad b_1^2 = \langle F_1|F_1\rangle \quad a_0 = \langle f_0|H|f_0\rangle$$

and, in general,

$$|F_{n+1}\rangle = H|f_n\rangle - a_n|f_n\rangle - b_n|f_{n-1}\rangle \quad n > 1. \quad (3)$$

The next pair of parameters b_{n+1}, a_{n+1} is given by the normalization of the state $|F_{n+1}\rangle$ and by the expectation value of the Hamiltonian on it, namely,

$$b_{n+1}^2 = \langle F_{n+1}|F_{n+1}\rangle \quad a_{n+1} = \langle F_{n+1}|H|F_{n+1}\rangle / \langle F_{n+1}|F_{n+1}\rangle. \quad (4)$$

After normalization of the state $|f_{n+1}\rangle = |F_{n+1}\rangle/b_{n+1}$, the steps (3) and (4) are repeated with n replaced by $n + 1$, and further functions of the hierarchy can be obtained. In the new basis $\{|f_n\rangle\}$ the Hamiltonian operator is represented by a tridiagonal Lanczos matrix T_M , which is then diagonalized, and whose elements $\{a_n\}$ and $\{b_n\}$ are explicitly known up to the order M ($M \leq N$) of the iteration performed.

Alternatively it is possible (and convenient when a large number of recursions is needed) to consider the continued fraction expansion of the diagonal Green function matrix element $G_{00}(E)$, whose coefficients are given by $\{a_n\}$ and $\{b_n^2\}$; we have

$$G_{00}(E) = \frac{1}{E - a_0 - b_1^2/[E - a_1 - b_2^2/(E - a_2 - \dots)]} \quad (5)$$

(the energy E is defined with a small imaginary part $+i\eta$, and the limit $\eta \rightarrow 0+$ is understood). In the case where the continued fraction (5) is truncated at a given level, the poles of the continued fraction give the eigenvalues of the system and their residua give the projected density of states, which is proportional to the absorption spectrum.

The procedure illustrated so far can be applied to perform the convolution between the two densities of states concerning the $E \otimes \varepsilon$ and $E \otimes \alpha_1$ systems. First of all it is easy to verify that the coefficients for the recursion for both the individual systems can be given in analytic form, taking as basis states the direct product of electronic and vibrational functions. In

particular for the $E \otimes \varepsilon$ system [13] we have

$$\begin{aligned} a_n^\varepsilon &= (n+1)\hbar\omega_\varepsilon & n &= 0, 1, \dots \\ b_n^{2,\varepsilon} &= nS_\varepsilon(\hbar\omega_\varepsilon)^2 & n &= 2, 4, \dots \\ b_n^{2,\varepsilon} &= (n+1)S_\varepsilon(\hbar\omega_\varepsilon)^2 & n &= 1, 3, \dots \end{aligned} \quad (6)$$

then

$$H_{JT,\varepsilon} = \sum_{n=0}^{\infty} a_n^\varepsilon |\xi_n\rangle\langle\xi_n| + \sum_{n=0}^{\infty} b_n^\varepsilon (|\xi_n\rangle\langle\xi_{n-1}| + |\xi_{n-1}\rangle\langle\xi_n|) \quad (7)$$

where $|\xi_n\rangle$ are the normalized functions of the recursion hierarchy for the $E \otimes \varepsilon$ system. For the $E \otimes \alpha_1$ system it is easily found that

$$\begin{aligned} a_n^{\alpha_1} &= (n + \frac{1}{2})\hbar\omega_{\alpha_1} \\ b_n^{2,\alpha_1} &= \frac{n}{2}k_{\alpha_1}^2 (\hbar\omega_{\alpha_1})^2 \end{aligned} \quad (8)$$

then

$$H_{JT,\alpha_1} = \sum_{n=0}^{\infty} a_n^{\alpha_1} |\zeta_n\rangle\langle\zeta_n| + \sum_{n=0}^{\infty} b_n^{\alpha_1} (|\zeta_n\rangle\langle\zeta_{n-1}| + |\zeta_{n-1}\rangle\langle\zeta_n|) \quad (9)$$

where $|\zeta_n\rangle$ are the normalized functions of the recursion hierarchy for the $E \otimes \alpha_1$ system.

Due to the commuting properties of the operators $H_{JT,\varepsilon}$ and H_{JT,α_1} , the energies and the intensities of the convoluted systems are

$$\begin{aligned} W_{p,i} &= E_p + e_i \\ I_{p,i} &\propto I_p^\varepsilon \times I_i^{\alpha_1} \end{aligned}$$

where E_p are the eigenvalues of the tridiagonal matrix (7) for the $E \otimes \varepsilon$ system, e_i are the eigenvalues of the shifted harmonic oscillator, that is $e_i = (i - S_{\alpha_1})\hbar\omega_{\alpha_1}$, and varying p and i all the eigenvalues of H_{JT} are obtained; I_p^ε indicates the intensity of the absorption $A \rightarrow E$ for the Jahn–Teller system $E \otimes \varepsilon$, and $I_i^{\alpha_1}$ has the well known Poisson shape ($I_i^{\alpha_1} = (S_{\alpha_1})^i e^{-S_{\alpha_1}}/i!$). Then we expect that the breathing mode acts to smooth the absorption spectrum of the $E \otimes \varepsilon$ Jahn–Teller system, and also to quench the cone resonances arising from a very strong Jahn–Teller coupling.

It is important to notice that the energies E_p and the intensities I_p^ε are easily obtained with high accuracy (the coefficients of the recursion are in analytic form) by diagonalizing the tridiagonal matrix or evaluating the poles of the corresponding continued fraction for a suitable number of steps.

3. Results for P_4^+ , As_4^+ and Sb_4^+

These calculations have been exemplified for the tetrameric cations P_4^+ , As_4^+ and Sb_4^+ , which can be pictured as strongly coupled $E \otimes \varepsilon$ Jahn–Teller systems and for which high resolution photoelectron spectra are available in the literature [15]. The energies of the phonon modes and the coupling constant are taken from the measurements of Wang *et al* [15]. The coupling constant for the α_1 mode is estimated from the profile of the $(2a_1)^{-1}$ bands of the photoelectron spectra shown in figures 1–3 of [15]. All the experimental data used in the calculations are summarized in table 1. Notice that, for these systems, the Jahn–Teller energy is very large; then the number of phonons to be taken into account is very large too, and so is the number of functions needed to give a satisfactory description of the

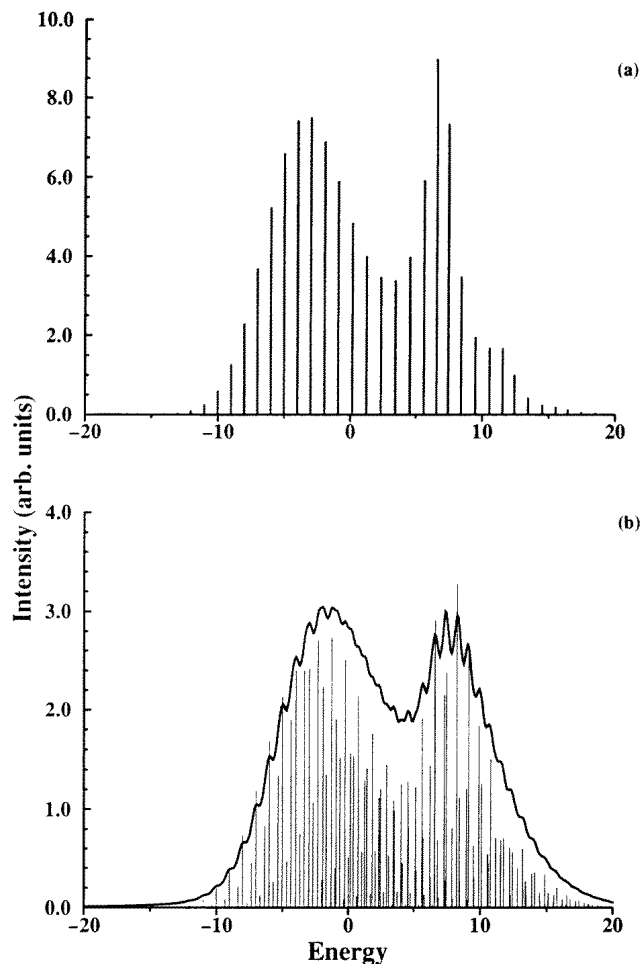


Figure 1. Eigenvalues, in units of $\hbar\omega_\varepsilon$, and peak intensities, in arbitrary units, for the cation P_4^+ with the parameters given in table 1: (a) vibronic system $E \otimes \varepsilon$; chain length $n = 450$; (b) vibronic system $E \otimes (\varepsilon + \alpha_1)$.

physical system. For instance, with a number of phonons for each phonon partner of the order of 1000, the number of basis functions (direct product of electronic and vibrational functions) is of the order of 10^6 , and any direct diagonalization is precluded. So the Lanczos technique, and in particular the possibility of having analytic coefficients of the recursion without numerical instabilities, is a very precious tool to calculate the energies and the intensities of these systems. In figures 1–3 we present the absorption peak intensity obtained for the vibronic $E \otimes \varepsilon$ and $E \otimes (\varepsilon + \alpha_1)$ Jahn–Teller systems and for the different cations, with the data given in table 1; the continuous line represents the broadening with a Lorentzian function of linewidth $\gamma = 0.4$. The quenching operated by the α_1 mode on the cone absorption spectra is evident. The ratio of the intensity of the two peaks and their separation are in good agreement with the experimental results.

We consider now the off-diagonal second-order terms in the $E \otimes \varepsilon$ Jahn–Teller system;

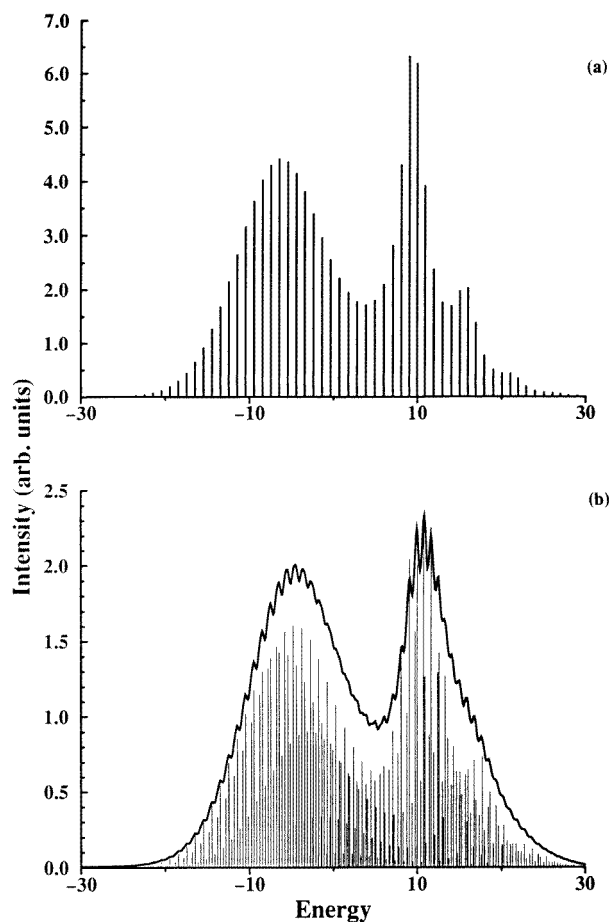


Figure 2. Eigenvalues, in units of $\hbar\omega_\varepsilon$, and peak intensities, in arbitrary units, for the cation As_4^+ with the parameters given in table 1: (a) vibronic system $\text{E}\otimes\varepsilon$; chain length $n = 1000$; (b) vibronic system $\text{E}\otimes(\varepsilon + \alpha_1)$.

Table 1. Energies of the phonon modes ε and α_1 in cm^{-1} and the corresponding dimensionless coupling constants for the different cations as from [15].

	P_4^+	As_4^+	Sb_4^+
$\hbar\omega_\varepsilon$	363	210	140
$\hbar\omega_{\alpha_1}$	606	344	241
k_ε	5.75	9.7	12.5
k_{α_1}	1.5	1.9	2.0

the Hamiltonian for the electron–phonon coupling has the form [7]

$$H_{\text{e-p}} = \hbar\omega_\varepsilon \begin{vmatrix} -k_\varepsilon q_1 + \frac{1}{2}g(q_1^2 - q_2^2) & k_\varepsilon q_2 + gq_1 q_2 \\ k_\varepsilon q_2 + gq_1 q_2 & k_\varepsilon q_1 - \frac{1}{2}g(q_1^2 - q_2^2) \end{vmatrix} \quad (10)$$

where g is the dimensionless second-order coupling constant.

The calculations are made in a second quantization scheme and using again the Lanczos

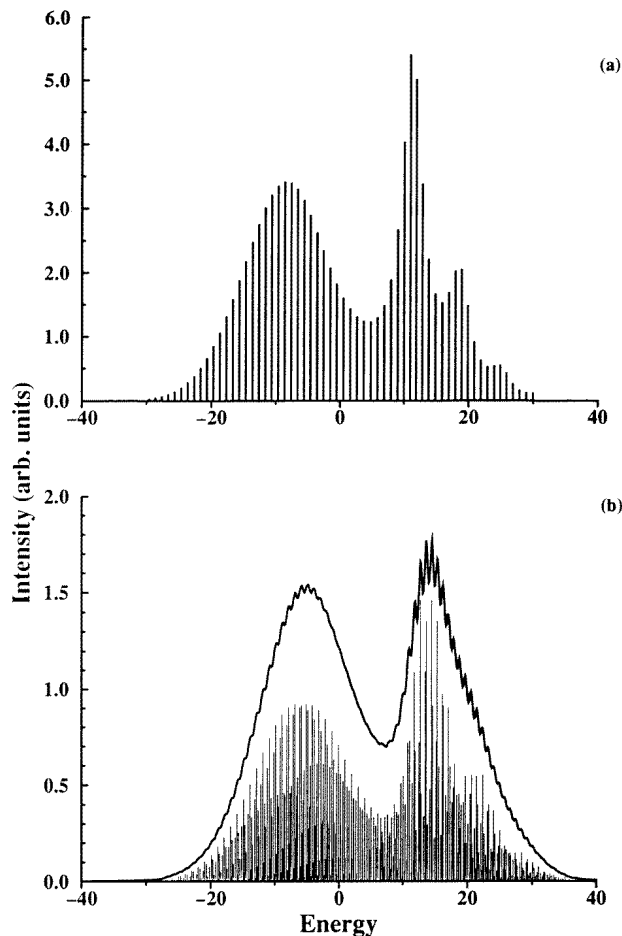


Figure 3. Eigenvalues, in units of $\hbar\omega_\varepsilon$, and peak intensities, in arbitrary units, for the cation Sb_4^+ with the parameters given in table 1: (a) vibronic system $E \otimes \varepsilon$; chain length $n = 1500$; (b) vibronic system $E \otimes (\varepsilon + \alpha_1)$.

technique, but in this case the coefficients of the recursion are no longer in analytic form. In the calculations we used at most 800 phonons for each phonon partner, and 2000 steps of the Lanczos chain. As usual in the Lanczos technique, at large numbers of iterations there are instabilities in the calculations of the recursion parameters due to the finite precision arithmetic of the computers, and spurious states can appear. Nevertheless we expect to obtain reasonably good spectral information [19], since the essential information is contained in the initial parameters of the chain. Even if the eigenvalues are not so precise as in the previous linear coupling case, their inaccuracy remains within a few per thousand. In effect we checked the convergence of the algorithm by means of the convergence parameter $W(E_i)$, defined [20] as the projection modulus squared of each eigenvector on the last state of the Lanczos chain. In our calculations and in the energy range of interest, $W(E_i)$ is, at most, of the order of 10^{-4} , and this means that we expect eigenvalues with at least three significant digits, enough to compare the calculations with the experimental results. Furthermore we have verified that the relative energy difference $[E(N) - E(N - 1)]/E(N)$, in the energy

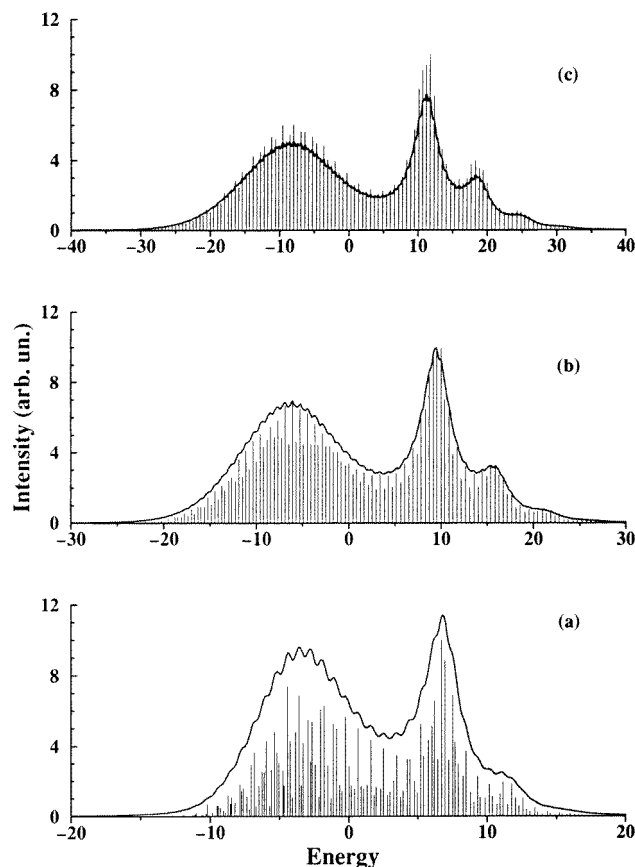


Figure 4. Jahn–Teller system $E \otimes \varepsilon$ with second-order effects. Eigenvalues, in units of $\hbar\omega_\varepsilon$, and peak intensities, in arbitrary units, of the tetrameric cations (a) P_4^+ , (b) As_4^+ and (c) Sb_4^+ . The parameters are those given in table 1; the second-order dimensionless coupling constant is $g = 0.3$. The continuous line represents the broadening with a Lorentzian function of linewidth $\gamma = 0.4$.

range of interest, is of the order of 10^{-3} with $N = 800$ for Sb_4^+ , less for the other cations considered.

The quadratic coupling constant g spans the interval $0 < g < 1$ (in this range we have no instabilities, as can be deduced looking at the lower adiabatic potential energy sheet [15]). In figure 4 we show the absorption spectra obtained for each tetrameric cation and with a second-order coupling constant $g = 0.3$, larger than usually considered [15, 16]. By inspection with figures 1(a), 2(a) and 3(a), it can be inferred that the bandshape is determined mostly by the linear Jahn–Teller interaction and that the second-order effect influences only marginally the cone resonances in these systems.

4. Conclusions

We have studied the vibronic model $E \otimes (\varepsilon + \alpha_1)$, with a very large linear interaction to the mode ε , applying the Lanczos recursion method to the $E \otimes \varepsilon$ system convoluted with a

Poisson function. Properly choosing the initial state, the coefficients of the recursion have been put in analytic form and the absorption spectrum has been calculated in a very reliable way. The calculations have been exemplified for the tetrameric cations P_4^+ , As_4^+ and Sb_4^+ and we have found a good agreement with the experimental results. Considering *separately* the effect of the off-diagonal second-order terms also, we have verified the role of the coupling to the totally symmetric mode for the quenching of the Slonczewski resonances in the strongly coupled $E \otimes \varepsilon$ Jahn–Teller systems.

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