

# Jahn-Teller Spectral Fingerprint in Molecular Photoemission: $C_{60}$

Nicola Manini\* and Paolo Gattari

*Dipartimento di Fisica, Università di Milano, Via Celoria 16, 20133 Milano, Italy  
and INFN, Unità di Milano, Milano, Italy*

Erio Tosatti

*International School for Advanced Studies (SISSA) and INFN Democritos National Simulation Center,  
Via Beirut 4, 34014 Trieste, Italy  
and International Centre for Theoretical Physics (ICTP), P.O. Box 586, 34014 Trieste, Italy  
(Received 28 July 2003; published 3 November 2003)*

The  $h_u$  hole spectral intensity for  $C_{60} \rightarrow C_{60}^+$  molecular photoemission is calculated at finite temperature by a parameter-free Lanczos diagonalization of the electron-vibration Hamiltonian, including the full 8  $H_g$ , 6  $G_g$ , and 2  $A_g$  mode couplings. The computed spectrum at 800 K is in striking agreement with gas-phase data. The energy separation of the first main shoulder from the main photoemission peak, 230 meV in  $C_{60}$ , is shown to measure directly and rather generally the strength of the final-state Jahn-Teller coupling.

DOI: 10.1103/PhysRevLett.91.196402

PACS numbers: 71.20.Tx, 33.20.Wr, 33.60.-q, 36.40.Cg

Photoemission (PE) from a closed-shell high-symmetry molecule, involving Jahn-Teller (JT) effect in the final state, is accompanied by characteristic vibronic structures in the measured hole spectrum [1]. Although accurate spectral calculations have recently appeared in the chemical literature, e.g., for benzene [2], there still is a strong need for a qualitative understanding of a more general nature, and informative on the nature and the strength of the JT-coupled problem. A recent case in point is that of gas-phase  $C_{60}$ , where an important side peak was reported 230 meV above the main PE peak [3,4] (see Fig. 1). As this excitation energy is in fact larger than all vibrational frequencies of  $C_{60}$  (32–197 meV), its nature could not be straightforwardly interpreted, leading to a debate [6].

In this Letter we present first of all a detailed understanding of the PE structures that are accurately reproduced for  $C_{60} \rightarrow C_{60}^+$  (Fig. 1) through calculations that fully include temperature and that contain no adjustable parameters. By taking further this calculation to pieces, we identify the important ingredients that determine the spectrum. The first is symmetry selection: the initial orbital symmetry dictated by the suddenly injected bare hole extends to the whole spectrum. The second is a property of weakly coupled JT vibronic multiplets that requires the first excitation energy of the same symmetry as the ground state (GS) to rise above the bare vibration energy by an amount strictly proportional to the squared JT coupling. Specifically in  $C_{60}^+$ , symmetry requires the 230 meV peak to correspond to an  $h_u$  vibronic excitation above the  $h_u$  GS. JT transforms the highest  $H_g^{(8)}$  vibration ( $\hbar\omega < 200$  meV) of  $C_{60}$  into an  $h_u$  vibron near 230 meV. Interestingly, the 20% magnitude of this upward shift fingerprints quite accurately the medium-sized overall JT coupling of  $C_{60}$ . As both properties above are apparently general, and since the upward shift tracks the cou-

pling intensity well beyond the weak-coupling limit, this kind of analysis appears of much more general value. In particular, the first vibronic excitation energy as seen in PE of other weak to medium JT-coupled molecules should and does gauge their respective couplings as well.

We adopt for  $C_{60}$  the simplest model [7–9] describing the JT coupling of the orbitally degenerate  $h_u$  hole with

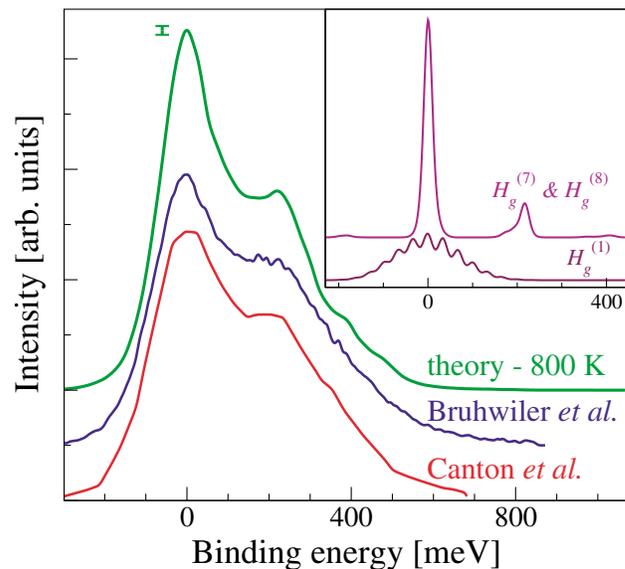


FIG. 1 (color online). Experimental PE spectra by Canton *et al.* [4] and by Brühwiler *et al.* [3] compared with the calculation based on the *ab initio* parameters of Ref. [5] ( $T = 800$  K,  $N_{\text{tier}} = 31$ ,  $N_{\text{max}} = 10^5$ ,  $N_{\text{sample}} = 245$ ). Intensities are normalized to unity. Inset:  $T = 800$  K spectra including the single  $H_g^{(1)}$  mode, and  $H_g^{(7)}$  and  $H_g^{(8)}$ . All spectra are shifted to move the main peak to zero energy and broadened with a 10 meV HWHM Gaussian. The error bar gives the largest statistical error introduced by random sampling of the initial states.

the molecular vibrations. The linear JT coupling is non-zero for two nondegenerate  $A_g$ , six fourfold-degenerate  $G_g$  and eight fivefold-degenerate  $H_g$  vibration modes, or 66 vibrations altogether [7,8,10]. The resulting  $h \otimes (A + G + H)$  JT Hamiltonian thus consists of the fivefold  $h_u$  highest occupied molecular orbital (HOMO), of 66 harmonic oscillators, and of the electron-vibration (e-v) coupling term [5,8]:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{vib}} + \hat{H}_{\text{e-v}}, \quad (1)$$

$$\hat{H}_0 = \epsilon_{\text{HOMO}} \sum_{m\sigma} \hat{c}_{m\sigma}^\dagger \hat{c}_{m\sigma}, \quad (2)$$

$$\hat{H}_{\text{vib}} = \frac{1}{2} \sum_{\Lambda j \mu} \hbar \omega_{\Lambda j} (\hat{P}_{\Lambda j \mu}^2 + \hat{Q}_{\Lambda j \mu}^2), \quad (3)$$

$$\hat{H}_{\text{e-v}} = \sum_{\substack{r \Lambda j \mu \\ \sigma m m'}} k^\Lambda g_{\Lambda j}^{(r)} \hbar \omega_{\Lambda j} C_{m-m'}^{r \Lambda \mu} \hat{Q}_{i \Lambda \mu} \hat{c}_{m\sigma}^\dagger \hat{c}_{m'\sigma}. \quad (4)$$

Here  $m, \mu$  label components within the degenerate multiplets [8,11],  $j$  counts modes of symmetry  $\Lambda$ ,  $C_{mm'}^{r \Lambda \mu}$  are Clebsch-Gordan coefficients [11] of the icosahedral group  $I_h$  that couple the  $h_u$  fermion operators  $\hat{c}_{m\sigma}^\dagger$  to a  $\Lambda$  vibration,  $\hat{Q}_{i \Lambda \mu}$  are the dimensionless normal-mode vibration coordinates in units of  $x_0(\omega_{\Lambda j}) = \sqrt{\hbar/(\omega_{\Lambda j} m_C)}$  where  $m_C$  is the mass of the C atom, and  $\hat{P}_{i \Lambda \mu}$  the corresponding conjugate momenta. The additional multiplicity  $r = 1, 2$ , needed for  $H_g$  vibrations only, labels the two separate kinds of  $H_g$  coupling allowed under the same symmetry [5,11].

In the present calculation we adopt the fully *ab initio* numerical values of the e-v coupling parameters  $g_{\Lambda j}^{(r)}$  obtained by a density functional (DF) calculation [5,12]. We also use the calculated vibrational frequencies of Ref. [5], that are close to the experimental frequencies of the  $A_g$  and  $H_g$  modes, but also cover the experimentally unavailable or unreliable  $G_g$  modes. e-v couplings are dimensionless, each of them normalized to its respective vibration quantum, so as to reflect directly the relative coupling strength. Numerical factors  $k^{A_g} = \frac{5^{1/2}}{2}$ ,  $k^{G_g} = \frac{5^{1/2}}{4}$ ,  $k^{H_g} = \frac{1}{2}$  are included to make contact with Ref. [5].

In the sudden approximation, the angle-integrated PE spectrum  $I(E)$  is given by Fermi's golden rule [2]

$$I(E) = \frac{1}{10} \sum_{m\sigma i} I_{im\sigma}(E) P(i), \quad (5)$$

$$I_{im\sigma}(E) = \sum_f | \langle f | \hat{c}_{m\sigma}^\dagger | i \rangle |^2 \delta(E - E_f + E_i), \quad (6)$$

where  $|i\rangle$  represents the starting vibrational eigenstate of neutral  $C_{60}$ , of energy  $E_i$ , and  $|f\rangle$  represents a vibronic JT eigenstate of  $C_{60}^+$ , of energy  $E_f$ .  $\hat{c}_{m\sigma}^\dagger |i\rangle$  is the initial bare hole, where the spin- $\sigma$  electron has been ejected from one orbital  $m$  of the fivefold-degenerate  $h_u$  HOMO, but the molecule is still unrelaxed. The factor 1/10 and the sum

over  $m$  and  $\sigma$  signify averaging over the five orbital and two spin states of the hole. Assuming thermal equilibrium we generate the boson numbers  $\{v_{\Lambda j \mu}\}$  of the initial neutral molecule by randomly sampling the probability distribution  $P(i) = Z^{-1} \exp(-E_i/k_B T)$ , where  $Z = \sum_i \exp(-E_i/k_B T)$  and  $E_i = \sum \hbar \omega_{\Lambda j} v_{\Lambda j \mu}$ . In the present medium-coupling regime we compute the final-state vibronic energies and matrix elements in (6) by numerical Lanczos diagonalization of the Hamiltonian (1) on the product basis of the five  $h_u$  states times the harmonic oscillator ladders. Since these contain an infinite number of states, some truncation is necessary. As we generally want to address high temperatures of the molecular beam ( $T = 800$  K used for  $C_{60}$ ,  $k_B T \geq 2\hbar\omega$  of the strongly coupled  $H_g^{(1)}$  mode) a standard truncation would involve a far too large Hilbert space size. We generate a smarter basis starting from the initial excitation  $\hat{c}_{m\sigma}^\dagger |i\rangle$ , and iteratively adding sets of states ("tiers") directly coupled to those of the previous tier by matrix elements of  $\hat{H}_{\text{e-v}}$ , in a scheme inspired by Ref. [14]. This procedure is iterated  $N_{\text{tier}}$  times so that states relevant at up to  $(2N_{\text{tier}})$ th order in perturbation theory are included [15]. The application of about 350 Lanczos steps [16] generates a tridiagonal matrix, which provides a well converged spectrum.

The basis for the calculation of Fig. 1 includes about 720 000 states, in particular, all the states generated by up to three applications of  $\hat{H}_{\text{e-v}}$  to  $\hat{c}_{m\sigma}^\dagger |i\rangle$ : the convergence of the truncated basis is quite good. We repeat the whole procedure of basis generation/spectrum calculation for each of the  $N_{\text{sample}}$  initial states, and average the obtained spectra. The above procedure is carried out including all  $H_g$  and  $G_g$  modes. The  $A_g$  modes separate out, as they can be solved analytically as a simple displaced oscillators, and are included exactly by convolution.

Figure 1 compares the theoretical PE spectrum calculated at  $T = 800$  K with the measured spectra by two separate groups. All experimental features, including the characteristically broad and asymmetric main PE peak, the strongest satellite peak around 230 meV, a second weaker peak near 400 meV, and a slow decay up to 600 meV, are remarkably reproduced, based purely on *ab initio* parameters. The model and its ingredients thus appear to describe quite accurately the PE spectrum of  $C_{60}$ . We can now take it apart, so as to understand the underlying physics to satisfaction.

We address the two main features of the spectrum, namely, (i) the large broadening and (ii) the 230 meV peak. By eliminating  $G_g$  and  $A_g$  modes from the calculation there is no large change in the spectrum. Thus only the  $H_g$  modes are important. Among  $H_g$  modes, the largest couplings belong to the low-frequency  $H_g^{(1)}$  32 meV quadrupolar radial mode, and to the two high-frequency C-C stretch modes  $H_g^{(7)}$  and  $H_g^{(8)}$  at  $\hbar\omega = 181$  and 197 meV. When we include  $H_g^{(1)}$  alone we find (inset of Fig. 1) that the thermally broadened asymmetric main peak is well reproduced. Therefore  $H_g^{(1)}$  is mainly responsible for the large spectral broadening.

When only  $H_g^{(1)}$  is included, all satellite structures above 200 meV are absent, and do not reappear even if we arbitrarily increase the  $H_g^{(1)}$  coupling to larger and larger values. This rules out the possibility to attribute the 230 meV structure to an “electronic” splitting [6]. As it turns out, electronic JT splittings become visible in experimental PE spectra, such as those of  $\text{Fe}(\text{CO})_5$  [17], and in theoretical spectra, like those of Martinelli *et al.* [18] only for very strong e-v coupling, whereas in  $\text{C}_{60}$  coupling is intermediate at most. This suggests that the 230 meV peak in  $\text{C}_{60}$  should rather be associated to the high-frequency modes  $H_g^{(7)}$  and  $H_g^{(8)}$ . However, the connection between their frequencies  $<200$  meV and the 230 meV peak position is far from obvious. To clarify this, we calculate the spectrum by including  $H_g^{(7)}$  and  $H_g^{(8)}$  alone (see inset of Fig. 1). The result is a much narrower spectrum ( $H_g^{(1)}$  is now omitted), showing a high-energy satellite at a significantly (10%) higher energy than  $\hbar\omega_{H_g,8}$ . This increase in vibronic excitation energy above the purely vibrational  $\hbar\omega$  for the  $\nu = 1$  phonon excitation of a trivial displaced oscillator is in fact a characteristic signature of the dynamic JT effect, and can be understood on the basis of symmetry. For  $H_g^{(7)}$  and  $H_g^{(8)}$ ,  $\hbar\omega$  is almost 3 times the thermal energy: the main initial-state contribution to the spectrum comes from  $|i\rangle =$  the neutral molecule GS, of symmetry  $A_g$ . The bare hole  $\hat{c}_{m\sigma}^\dagger|i\rangle$  therefore carries the orbital  $h_u$  symmetry of the HOMO. This state has nonzero overlap strictly only with final states  $|f\rangle$  of the same symmetry  $h_u$ . This *single symmetry channel* thus represents the only contributor to the low-temperature PE spectrum according to (6) [19]. The blueshift of the vibronic peak relative to the bare vibration is now due to two general properties (in fact common to all dynamical JT systems): (i) the coupling independence of the *average* excitation energy in any vibronic multiplet at weak coupling (the leading change is of order  $g^4$ ) [20], and (ii) the increasing “repulsion” that the GS level exerts for increasing  $g$  on all excited states of the same symmetry, which pushes them upward.

Both concepts are illustrated in Fig. 2, depicting the vibronic excitation energies (with special attention to the  $h_u$  states) for the simplest case of a single  $H_g$  mode, as a function of the e-v coupling strength  $g^2$ . The approximate coupling independence of the average excitation energy of the multiplet of states derived from the  $\nu = 1$  phonon manifold is apparent. Within this multiplet (made of  $h_u \times H_g = a_u + t_{1u} + t_{2u} + 2g_u + 2h_u$ ), the  $h_u$  vibronic states are the only ones that have another state of the same symmetry (the GS itself) lower in energy “pushing” them upward. As a result, for small but increasing coupling, the  $h_u$  excited vibronic states move necessarily upward in energy above  $\hbar\omega_{H_g}$ . Moreover, the amount of shift is at weak coupling proportional to  $g^2$  and reflects the strength of the coupling. None of these results seem specific to the  $h \otimes H$  JT model of  $\text{C}_{60}$ . For example, identical conclusions apply to the  $e \otimes E$  problem [20]. Indeed, a 15% blueshift of the

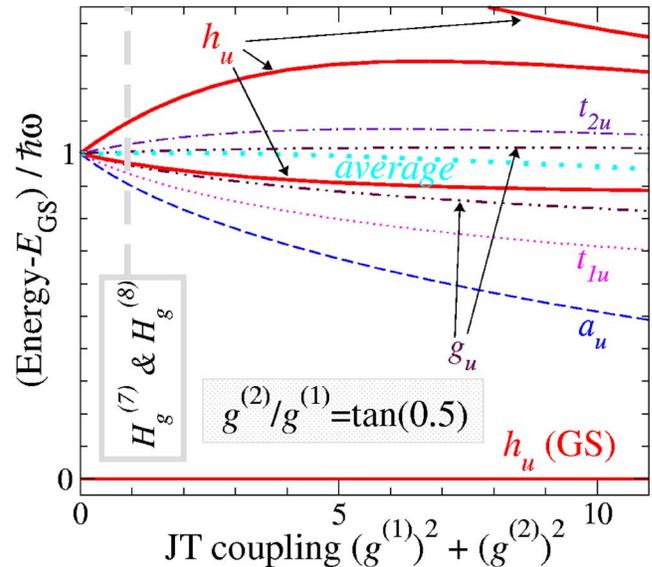


FIG. 2 (color online). Vibronic excitation energies for a single  $H_g$  mode coupled to the  $h_u$  level, as a function of coupling, for a ratio  $g^{(2)}/g^{(1)}$  characteristic of the  $H_g^{(7/8)}$  modes. The *average* refers to the multiplet originating from the one-phonon states. Bold:  $h_u$  states, the only visible states in  $T = 0$  PE.

first vibronic satellite is clearly observable in the PE spectra of benzene [21].

In  $\text{C}_{60}$  we must consider the two high-frequency modes  $H_g^{(7)}$  and  $H_g^{(8)}$  at  $\hbar\omega = 181$  and 197 meV. The couplings for these two modes alone account for a 10%, or roughly 20 meV, shift of the main  $H_g^{(7/8)}$  vibronic satellite above  $\hbar\omega$ . This is about half of the total observed and calculated shift of  $\sim 40$  meV of the 230 meV satellite relative to  $\hbar\omega$ . The remainder is a collective effect of all other modes simultaneously interacting with the HOMO, and pushing their respective  $\nu = 1$  satellites (weak and thus invisible at large temperature) upward. All goes as if effectively the coupling of the  $H_g^{(7/8)}$  modes were larger, i.e., effectively moving to the right of the vertical dashed line in Fig. 2.

We have thus attained the following understanding of the 800 K PE spectrum of  $\text{C}_{60}$ : (i) the strong 230 meV satellite (and the weak 400 meV) is due to  $h_u$ -symmetry vibrons derived from  $H_g^{(7/8)}$  modes, blueshifted by repulsive coupling to the  $h_u$  GS, and (ii) the large spectral broadening is due mainly to  $H_g^{(1)}$ . Clearly, this broadening of the 800 K spectrum prevents direct extraction of further detailed information about the actual e-v couplings of the fullerene cation. Our calculations, when repeated for lower temperatures, indicate a wealth of structures that should emerge. Figure 3 shows that already a measurement carried out at 300 K would provide enough detail to get precise indications about the couplings of individual modes. For example, the intensity ratio between the main peak and the subsequent peaks at 35 and 65 meV is a direct measure of  $g_{H_g,1}$ . A cool molecular beam experiment would be extremely useful.

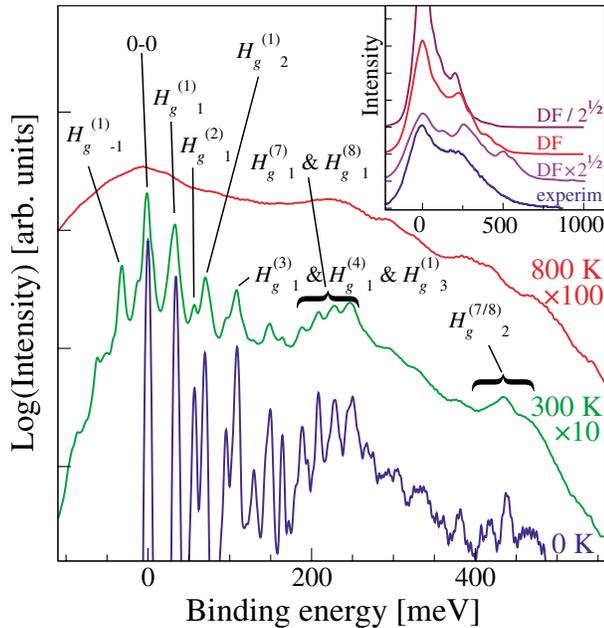


FIG. 3 (color online). Temperature dependence of the PE, computed including all modes of  $C_{60}$  for  $T = 0$ ,  $T = 300$  K, and  $T = 800$  K. Labels  $\Lambda_v^{(j)}$  indicate the leading component in the vibronic states. Inset: computed spectra ( $T = 800$  K) based on the same DF coupling parameters  $g_{\Lambda_j}^r$  divided by  $\sqrt{2}$ , original, and multiplied by  $\sqrt{2}$ , compared to experiment [3].

Also in view of future cool-beam data it is meaningful to address the question of how accurate the calculated DF e-v couplings used here really are. For  $t_{1u}$  electrons coupled to  $H_g$  vibrations, the calculated DF couplings were argued, for example, to be too weak by a substantial amount, by comparison to the larger couplings needed in order to fit  $C_{60}^-$  PE [22]. In our HOMO case, the excellent agreement of calculations with experiment suggests that there is no such failure. Figure 3 (inset) shows several PE calculations with rigidly rescaled e-v parameters. Comparison with experiment indicates that the DF couplings are, on the whole, quite close (if slightly on the weak side) to the actual couplings of  $C_{60}^+$ . Much larger JT coupling values—like those obtained using different approaches [23]—are ruled out, as they would produce excessive blueshift of the  $H_g^{(7/8)}$  satellite. This is very good news, for it gives further confidence in the future possibility to rely solidly on DF for a good description of the intrafullerene chemical bond, and of its perturbations.

In conclusion, we present here a detailed calculation of the PE spectrum of a high-symmetry molecule,  $C_{60}$ , which is JT active in its one-hole state. We find excellent agreement with experiment, confirming for the first time the accuracy of the e-v couplings as extracted from DF calculations. Perhaps more importantly, we reach a fresh understanding of the PE spectrum, with its width, its vibronic peak, and the reason for its blueshift relative to the bare vibrations. The blueshift of the one-

vibron satellite is argued to represent a more general characteristic fingerprint of JT systems in the weak-to-intermediate coupling regime, and is found, for example, in the  $e \otimes E$  JT of benzene as well.

We are indebted to G. P. Brivio, P. Brühwiler, A. Del Monte, D. Galli, M. Lueders, L. Molinari, G. Onida, F. Parmigiani, A. Parola, and G. E. Santoro for useful discussion. This work was supported by the European Union, Contracts No. ERBFMRXCT970155 (TMR FULPROP) as well as by MIUR COFIN01, and FIRB RBAU017S8R operated by INFN.

\*Electronic address: nicola.manini@mi.infn.it

- [1] R. Lindner *et al.*, *Science* **271**, 1698 (1996).
- [2] H. Köppel *et al.*, *J. Chem. Phys.* **117**, 2657 (2002).
- [3] P. Brühwiler *et al.*, *Chem. Phys. Lett.* **279**, 85 (1997).
- [4] S. E. Canton *et al.*, *Phys. Rev. Lett.* **89**, 045502 (2002).
- [5] N. Manini *et al.*, *Philos. Mag. B* **81**, 793 (2001).
- [6] N. Manini and E. Tosatti, *Phys. Rev. Lett.* **90**, 249601 (2003); S. E. Canton *et al.*, *ibid.* **90**, 249602 (2003).
- [7] A. Ceulemans and P. W. Fowler, *J. Chem. Phys.* **93**, 1221 (1990).
- [8] N. Manini and P. De Los Rios, *Phys. Rev. B* **62**, 29 (2000).
- [9] C. P. Moate *et al.*, *Phys. Rev. Lett.* **77**, 4362 (1996).
- [10] M. Lüders *et al.*, *Philos. Mag. B* **82**, 1611 (2002).
- [11] P. H. Butler, *Point Group Symmetry Applications* (Plenum, New York, 1981).
- [12] Another DF calculation [13] based on a different functional yielded couplings roughly in the same range. However, we could not recompute the PE spectrum with these couplings due to their lack of distinction between coupling contributions of type  $r = 1$  and  $r = 2$ .
- [13] M. Saito, *Phys. Rev. B* **65**, 220508 (2002).
- [14] A. A. Stuchebrukhov and R. A. Marcus, *J. Chem. Phys.* **98**, 6044 (1993).
- [15] The tier size increases quickly, but we cut it off by including up to some given number  $N_{\max}$  of states per tier, according to their perturbative weight  $w_b = \sum_a f(\langle b | \hat{H}_{e-v} | a \rangle [E_a - E_b]^{-1}) w_a$  where  $f(x) = (1 + x^2)^{-1/2}$ , the sum extends over all the states  $|a\rangle$  in the previous tier, and the weight of  $\hat{c}_{m\sigma}^\dagger |i\rangle$  is unity.
- [16] J. Jaklic and P. Prelovsek, *Adv. Phys.* **49**, 1 (2000).
- [17] J. L. Hubbard and D. L. Lichtenberger, *J. Chem. Phys.* **75**, 2560 (1981).
- [18] L. Martinelli *et al.*, *Phys. Rev. B* **43**, 8395 (1991).
- [19] This, incidentally, rules out the possibility to observe tunnel split states [4] in PE, as they necessarily possess different symmetries.
- [20] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, Berlin, 1989), Sec. 4.1.
- [21] P. Baltzer *et al.*, *Chem. Phys.* **224**, 95 (1997).
- [22] O. Gunnarsson *et al.*, *Phys. Rev. Lett.* **74**, 1875 (1995); O. Gunnarsson, *Phys. Rev. B* **51**, 3493 (1995).
- [23] R. D. Bendale *et al.*, *Chem. Phys. Lett.* **194**, 467 (1992).