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Optical properties of one-dimensional π-conjugated compounds: Study of the pressure-dependent linear properties of K-tetracyanoquinodimethane

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The pressure-dependent optical conductivity spectra of K-TCNQ (tetracyanoquinodimethane) single crystals, a well characterized one-dimensional electron-correlated system, are interpreted on the basis of a Holstein-Hubbard model. The effect of increasing pressure on both electronic and vibronic excitations is accounted for by considering an increasing average value of the transfer integral ($\bar{t}$) and of the nearest-neighbor electron-electron interaction (V). It is also shown that the pressure induces a decrease of the one-dimensional dimerization of the radical stacks and that the electron-electron correlation energy is always of the same order as the bandwidth.

I. INTRODUCTION

Charge-transfer (CT) molecular crystals form a class of π-conjugated systems with a great variety of structural and electronic characteristics. In particular one finds compounds that differ for the dimensionality of the relevant interactions (from one to three), the average number of electrons per molecular site (half-filled, quarter-filled, ... systems), the presence of intramolecular and/or intermolecular distortions and the possibility of equal or different site energies.[1] CT molecular compounds can be obtained as good crystals and, therefore, the measurement of their optical properties gives reliable experimental data. Furthermore, the above recalled structural and electronic features allow one to compare fruitfully their properties with those of the organic π-conjugated polymers. This class of compounds is under intense experimental and theoretical investigations because of direct technological interest in their properties such as the nonlinear optical behavior, which is promising for application in the field of photonics.[2,3] In fact, most important organic π-conjugated polymers can be considered as one-dimensional, half-filled, dimerized or tetramerized structures and, therefore, can be theoretically compared with corresponding CT molecular systems.

A CT molecular crystal that has been well characterized from the structural point of view and for which good linear optical data are available, is K-TCNQ (TCNQ=tetracyanoquinodimethane). At room temperature and pressure, this molecular compound is a one-dimensional, half-filled and dimerized system made up of stacks of radical anion TCNQ molecules all with the same site energy.[4] Parallel chains of potassium cations determine the electrical neutrality of the crystal. The optical data are available both for the dimerized structure at room temperature and for the regular one at high temperature ($T \geq 395$ K) and show electronic and vibronic excitations that strongly depend on the presence of the dimerization of the stacks.[5,6]

The study of the properties of CT crystals, as well as of π-conjugated polymers, has to face the problem of considering the electron-electron interaction which, for these systems, is not negligible with respect to the bandwidth energies.[7] Therefore, in calculating the optical properties one should explicitly consider the correlation between electrons. The Hubbard model has been found appropriate for an approximate description of such an interaction, however, the optical responses of an infinite system of this simple model are not available.

A Holstein-Hubbard model, which also includes the dynamic interaction of intramolecular vibrations with electrons, made up of four sites in a ring configuration with periodic boundary condition ($4S$ ring), has been shown to give a correct qualitative and quantitative interpretation of the linear optical data of a CT crystal such as K-TCNQ, also as a function of the dimerization of the stacks.[8] The success in the interpretation of the optical data has been related to the fact that the $4S$-ring model describes states corresponding to those at $k = 0$ and at $k = \pi/(2d)$ of a one-dimensional dimerized infinite chain.

As mentioned above, the same model can also be used for describing optical properties of polymers with the same type of structural and electronic features. One important example to compare to K-TCNQ is polyacetylene, the prototype of π-conjugated polymers. For this compound both linear optical data and nonlinear frequency-dependent third-harmonic-generation (THG) data at room temperature and pressure are available. The $4S$-ring model accounts for both linear and THG spectra of polyacetylene[9] and it has been shown how the dimerization of the system is important in determining the optical response, an issue that, for π-conjugated systems, has been recently put in evidence also from the experimental point of view.[10]

Qualified optical data of a K-TCNQ single crystal as a function of pressure have been recently published.[11] The data show that the pressure induces a clear decrease of the energy of the lowest CT excitation observed in the near-infrared linear spectrum. Futhermore, there are also indications of the intensity variation of the two CT bands and of the vibronic features observed in the near-infrared and infrared spectrum, respectively. Previously, a small shift of the frequency of the main CT band of powders of K-TCNQ was observed as a function of pressure.[12] Although the frequency shift is different in the two studies, which used different pressure transmitting media, one notes that the shift is toward lower values in both cases. Other pressure-dependent measurements on K-TCNQ powders recorded frequency shifts of the vibrational modes.[13]

The recent pressure-dependent optical data,[11] which will be discussed in the following, were interpreted with a qualitative analysis[11] on the basis of an approximate model that accounts for very strong electron interactions.[14] However, as also recognized in the same paper,[11] the real situation for K-TCNQ is quite different, since the electron correlation are of the order of the bandwidth. In the following sections it will be shown how the analysis of the data based on the $4S$-ring model can be developed to obtain a new qualitative insight and a quantitative analysis.

II. MODEL CALCULATIONS

The Hamiltonian for the Holstein-Hubbard $4S$-ring model is:

$$H = H_e + H_v + H_{e\text{-}v}. \tag{1}$$

H_e is the extended-Hubbard electronic part and can be written

$$\begin{aligned} H_e = & -\sum_{n=1}^{4}\sum_{\sigma} t_{n,n+1}(a^\dagger_{n,\sigma}a_{n+1,\sigma} + a^\dagger_{n+1,\sigma}a_{n,\sigma}) \\ & + U\sum_{n=1}^{4} n_{n,\sigma}n_{n,-\sigma} + \sum_{n=1}^{4} V_{n,n+1}n_n n_{n+1} \ , \end{aligned} \tag{2}$$

where $n_n = \sum_\sigma n_{n,\sigma}$, $n_{n,\sigma} = a^\dagger_{n,\sigma}a_{n,\sigma}$, and $a^\dagger_{n,\sigma}(a_{n,\sigma})$ is the creation (annihilation) operator for an electron with spin $\sigma = \uparrow, \downarrow$ on site n. $t_{n,n+1}$ is the charge-transfer parameter, U describes the intramolecular Coulomb interaction, and $V_{n,n+1}$ the nearest-neighbor intermolecular one. Because of the ring configuration, the site $n+1 = 1$ when $n = 4$.

H_v is the vibrational Hamiltonian in the harmonic approximation for an arbitrary number of intramolecular modes α

$$H_v = (\hbar/4)\sum_{n=1}^{4}\sum_{\alpha}\omega_\alpha(P^2_{n,\alpha} + Q^2_{n,\alpha}) \ , \tag{3}$$

where $Q_{n,\alpha}$ are the dimensionless coordinates for the intramolecular vibrations of frequency ω_α of site n and $P_{n,\alpha}$ the corresponding momenta.

$H_{e\text{-}v}$ describes the interaction between the intramolecular vibrational coordinates and the electronic degrees of freedom

$$H_{e-v} = \sum_{\alpha} g_\alpha Q_{n,\alpha} n_n \ , \tag{4}$$

where $g_\alpha = \left(\partial\epsilon_n/\partial Q_{n,\alpha}\right)_{\text{o}}$ and ϵ_n is the site energy, equal for all sites.

The optical functions are obtained by solving H_e on the basis of a valence bond scheme and then including the perturbing effects of the vibrations and of an electric field.[8] One notes that the solution of the electronic Hamiltonian is exact since the electron-correlation terms are considered without approximations.

From the expression for the frequency-dependent optical conductivity one can obtain useful expressions for the intensity and frequency of the electronic and vibronic excitations of the spectrum.[8] For an electronic CT excitation at $\hbar\omega_{\mathrm{CT}_j}$ one finds that its intensity is

$$I_{\mathrm{CT}_j} = e^2\pi N\frac{|v_{fj}|^2}{\hbar\omega_{\mathrm{CT}_j}} \ , \tag{5}$$

where $v_{fj} = \langle f|v|j\rangle$ and v is the velocity operator for the periodic dimerized $4S$ ring. $|f\rangle$ is the ground state and $|j\rangle$ an excited state of the electronic Hamiltonian H_e. N is the number density of tetramers. For the vibronic intensity (I_{ir}) and the perturbed frequency (ω_{ir}) of a vibration with frequency ω_α one finds

$$I_{ir} = e^2\pi N g_\alpha^2\hbar\omega_\alpha\left(\sum_j\frac{iv_{fj}\mathcal{V}_{fj}}{\hbar^2\omega^2_{\mathrm{CT}_j}}\right)^2 \ , \tag{6}$$

$$\omega_{ir} = \omega_\alpha\left[1 - \frac{g^2_\alpha}{\hbar\omega_\alpha}\sum_j\frac{|\mathcal{V}_{fj}|^2}{\hbar\omega_{\mathrm{CT}_j}}\right]^{\frac{1}{2}} \ , \tag{7}$$

where $\mathcal{V}_{fj} = \langle f|\delta_+|j\rangle$ and $\delta_+ = (n_1-n_2)+(n_3-n_4)$ is the electronic operator coupled to the out-of-phase combination of intramolecular vibrations of the unit cell molecules of the dimerized system. For a molecule such as TCNQ, whose symmetry does not allow a degenerate electronic ground state, the vibrations with $g_\alpha \neq 0$ are the totally symmetric modes that are infrared inactive for the isolated molecule and can be observed in the infrared spectra with a strong intensity only as a consequence of their interaction with CT excitations.

The above expressions can be used to obtain a synthetic view of the optical excitations of the $4S$-ring model as a function of the values of the parameters. In particular, for understanding the variation of the frequency-dependent conductivity induced by a hydrostatic pressure, one has to consider, in particular, the effect of the shortening of the average distance between molecules. For K-TCNQ a shortening of the average intrastack molecular distance would induce an increase of the average charge-transfer parameter $\bar{t}$ and an increase of the intermolecular Coulomb interaction V. Furthermore, one should also consider that the extent of dimerization of the stacks could change.

Figures 1 and 2 show the influence of a variation of $\bar{t}$ and V, respectively, on the intensity and energy of the CT and vibronic excitations. The figures also show the

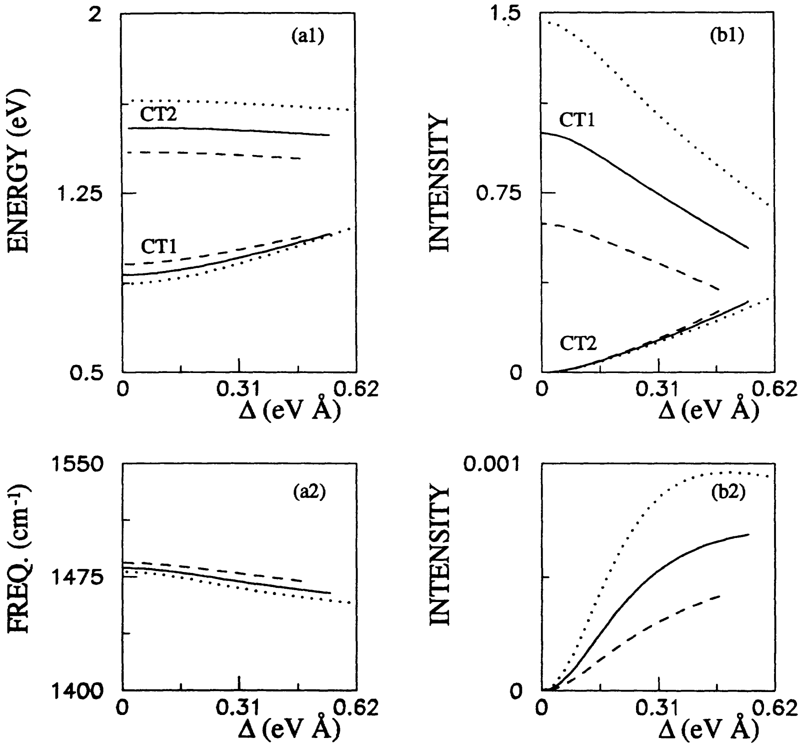

FIG. 1. Energies and intensities of the calculated electronic [(a1) and (b1)] and vibronic [(a2) and (b2)] excitations of the Holstein-Hubbard 4S-ring model as a function of the dimerization $\Delta = |t_1 d_1 - t_2 d_2|$. The three types of lines refer to calculations that differ only for the average value of the charge-transfer integral $\bar{t}$. $\bar{t}$ is 0.20, 0.16, and 0.24 eV for the calculations reported as continuous, dashed, and dotted lines, respectively. See the text for the values of the other parameters. CT1 and CT2 indicate the two most important electronic excitations of the 4S-ring model (see the text). Note that all the intensities are scaled to that of CT1 for the regular phase ($\Delta = 0$).

dependence of these excitations on the dimerization $\Delta = |t_1 d_1 - t_2 d_2|$ (d_i is a distance between molecules whose charge-transfer interaction is t_i). The two CT excitations reported in the figures are those with lowest frequency among the calculated ones and previously called CT1 and CT2.[8] It has been shown that these are the only ones that have to be considered for describing the spectra of CT molecular solids such as K-TCNQ.[8]

The excited states related to CT1 and CT2 are the first and the second B_u state, respectively, of the 4S ring and can be described as states where a transfer of one electron from nearest-neighbor sites occurred. One

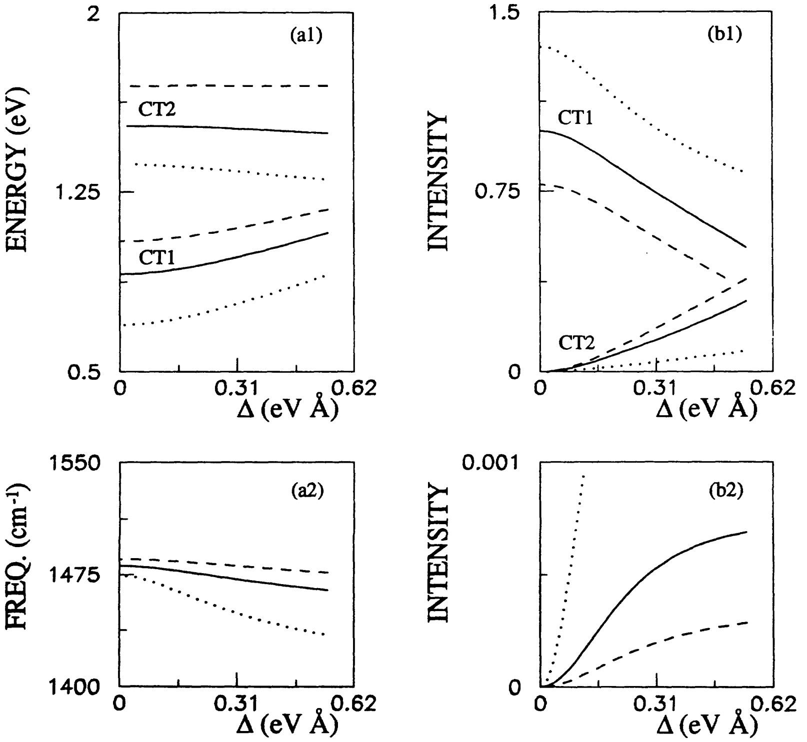

FIG. 2. Same as Fig. 1 but for calculations in which $\bar{t}$ is 0.20 eV and the nearest-neighbor V is varied. V is 0.2, 0.0, and 0.4 eV for the calculations reported as continuous, dashed, and dotted lines, respectively.

finds that these excited states have excitonic nature as it can be deduced by calculating the correlation function[15] $(1/\mathcal{N})\langle\sum_i(n_i-1)(n_{i+l}-1)\rangle$ as a function of l, where $\mathcal{N}$ is the number of sites. On the other hand the A_g ground state is found to be a covalent state with a dominant contribution of configurations with one electron per site and antiferromagnetically ordered spins.

The data reported in Figs. 1 and 2 as continuous lines are those of Fig. 3 of Ref. 8 and are calculated using values of the parameters that are characteristic of a CT solid: $U = 1.4$ eV, $V = 0.2$ eV, the frequency of the vibration $\omega_\alpha = 1500\ \mathrm{cm}^{-1}$ and its coupling constant $g_\alpha =$ 0.1 eV; $t_1 = 0.1$ eV, $t_2 = 0.3$ eV, $d_1 = 3.0$ Å, and $d_2 =$ 3.5 Å where the dimerization Δ is 0.55 eV Å. The values of t_i and d_i are varied linearly to the final values $t =$ 0.2 eV and $d = 3.25$ Å where $\Delta = 0$. All the intensities are scaled to the value of the more intense CT excitation of the regular stack system. Parts (a1) and (b1) report the energy and intensity of CT1 and CT2 whereas parts (a2) and (b2) report those of the vibronic excitation.

In Fig. 1 continuous lines show the calculation in which $\bar{t} = 0.2$ eV, while dashed and dotted lines show calculations in which $\bar{t} = 0.16$ eV and $\bar{t} = 0.24$ eV, respectively. The values of t_i and d_i for the largest Δ are evaluated on the basis of the linear variation of the values of these parameters for the case of $\bar{t} = 0.2$ and are $t_1 = 0.08$ eV, $d_1 = 3.55$ Å, $t_2 = 0.24$ eV, and $d_2 = 3.15$ Å ($\Delta = 0.472$ eV Å) for the calculations with $\bar{t} = 0.16$ and $t_1 = 0.12$ eV, $d_1 = 3.45$ Å, $t_2 = 0.36$ eV, and $d_2 = 2.85$ Å ($\Delta = 0.612$ eV Å) for the calculations with $\bar{t} = 0.24$.

In Fig. 2 continuous lines refer to the calculation in which $V = 0.2$ eV, while dashed and dotted lines show calculations in which $V = 0.0$ eV and $V = 0.4$ eV, respectively. Small differences are found when V is considered to be proportional to $1/d$.

Some general features of the results, in particular their dependence on the dimerization, were already described.[8] One briefly recalls that there is only one CT band for the regular system (CT1) because the intensity of CT2 vanishes and that the vibronic bands are present only for the dimerized phase. These and other features of the calculated spectra can be experimentally observed in the temperature-dependent spectra of K-TCNQ, which is an example of spectra that depend on dimerization.[5,6]

Other features of the reported calculations should now be observed. The intensity of CT1, the CT transition at lower frequency, is increased by a larger value of both $\bar{t}$ and V, but its energy is mainly influenced by a variation of the value of V. For CT2 one finds that its intensity is influenced by a change in the value of V but not of $\bar{t}$. On the other hand the energy of CT2 is affected in an opposite way by a change of $\bar{t}$ or of V. For the vibronic band one finds that its intensity is strongly modified by a variation of V and less by a variation of $\bar{t}$, whereas the perturbation of its frequency is particularly determined only by a decreasing V.

The behavior of the vibronic band can be understood looking at the behavior of the charge-transfer bands, in particular of CT1. A lower frequency of such a band determines an increase in intensity of the vibronic band and a lowering of its frequency. Other features, such as the behavior of CT1, can be understood if one assumes that its intensity is mainly determined by $(U-V)/(4\bar{t})$ and its energy by $(U-V)$.

III. PRESSURE-DEPENDENT OPTICAL SPECTRA OF K-TCNQ

The main features of the pressure-dependent optical conductivity of K-TCNQ can be summarized by recalling the frequency and intensity dependence of the two observed CT bands and of one vibronic band.[11] The A and B CT bands, which were previously identified as CT1 and CT2, respectively,[8] behave in a different way. One observes, for an increasing pressure, a decrease of the frequency of the A band (CT1) but not of the B band (CT2), whose frequency remains almost unchanged. On the other hand, the intensity of both CT bands is observed slightly to decrease as can be calculated from the integrated intensity $[I_{L_i} = (\pi/2)\alpha_i\omega_i^2]$ of the Lorentzian functions $[\epsilon_i(\omega) = \epsilon_\infty + 4\pi\alpha_i\omega_i^2/(\omega_i^2-\omega^2-i\Gamma_i\omega)]$ used for their description.[11] For the representative vibronic band at 1580 cm^{-1} (a_g ν_3) it was found that its intensity is almost independent of pressure. Data for its frequency have not been reported.[11]

The most evident change of the spectrum is the lower frequency of the A band (CT1) for high pressure. Looking at Figs. 1 and 2 one observes that this effect can be obtained with an increase both of the average value of the transfer integral $\bar{t}$ and of the intermolecular Coulomb interaction V. And, as previously recalled, this is in agreement with the effect the pressure would induce on a solid such as K-TCNQ. These variations are also in agreement with the fact that one does not observe a frequency shift of the B band (CT2). In fact, the effect of a variation of $\bar{t}$ on the frequency of CT2 is opposite to that of V (see Figs. 1 and 2).

For what concerns the intensities, one first observes that a constant intensity of a vibronic band does not mean that the dimerization of the system is unchanged.[11] This is particularly evident (see Figs. 1 and 2) when there is a lowering of the frequency of CT1 as experimentally found. In this case, for a constant dimerization one would expect an increase of the vibronic intensity. Therefore, the experimental data, which show an almost constant intensity of the vibronic band, point to a decrease of the dimerization of the system.

On the other hand, one expects that an increase of $\bar{t}$ and of V also determines an increase of the overall intensity of the spectrum as is clear from the data of Figs. 1 and 2. This result is also expected on the basis of analytical exact results for an infinite, half-filled, and regular Hubbard chain.[16] In fact it was shown that the overall intensity of the CT excitations depends on $U_{\mathrm{eff}}/(4\bar{t})$, where U_{eff} is the energy for obtaining a double occupancy of a site, which, in the case one also considers V, is $(U-V)$. Both a higher value of $\bar{t}$ and V determines a lower value of $U_{\mathrm{eff}}/(4\bar{t})$ which causes a higher intensity of the spectrum. Therefore, by assuming that $\bar{t}$ and V are increased by pressure, it is not clear why the experimental optical conductivity data do not show an increase of the overall

TABLE I. Values of the parameters used for the calculations of Fig. 3. R.P. and H.P. refer to the room pressure (continuous line) and high pressure (dashed line), respectively. $U = 1.33$ eV and $10^{-20}N = 8.929$ cm^{-3} for both calculations. $\bar{t}$, V, t_1, t_2, Γ_{CT_1}, Γ_{CT_2}, g_α are in eV, d_1 and d_2 in Å, Δ in eV Å, γ_α and ω_α in cm^{-1}.

	$\bar{t}$	V	t_1	d_1	t_2	d_2	Δ	Γ_{CT_1}	Γ_{CT_2}	ω_α	g_α	γ_α
R.P.	0.215	0.28	0.12	3.567	0.31	3.237	0.575	0.13	0.24	1608	0.91	7
H.P.	0.230	0.38	0.19	3.445	0.27	3.306	0.238	0.20	0.10	1623	0.91	14

intensity. However, one observes that the reported experimental conductivity spectrum[11] has been obtained from reflectivity data that have not been normalized. And a different integrated intensity of the conductivity spectrum can be obtained when reflectivity data have different absolute values. Therefore, the present fitting of the experimental data does not give particular importance to the reported intensity of the CT bands.

There are no definite rules for modifying the values of the parameters of the model as a function of pressure. However, the unperturbed frequency ω_α of the a_g ν_3 vibration is experimentally observable in the pressure-dependent Raman spectra of K–TCNQ (Ref. 13) and one finds that a_g ν_3 has a positive frequency shift of about 3 cm^{-1} GPa^{-1}. For what concerns the value of the other parameters one chooses to let unchanged the density of tetramers (N) since there is a linear dependence of the conductivity function on N and the variation of such value is probably of minor importance. On the other hand, the variation of t_i and d_i is considered to be linear and consistent with the value of these parameters obtained from the fitting of the room pressure spectrum.[8] Without additional information one also chooses not to vary the value of the vibronic coupling constant g_α.

In Fig. 3 are shown the calculated conductivity spectra for K-TCNQ at high pressure (4.91 GPa) (solid line) and at room pressure (dashed line). The values of the parameters used for the two calculations are reported in Table I.

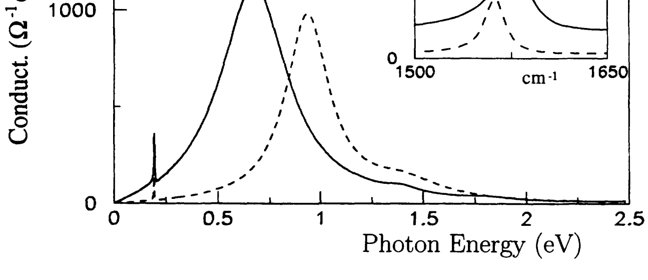

FIG. 3. Calculated conductivity spectra for K-TCNQ at 4.91 GPa (continuous line) and at room pressure (dashed line). The vibronic part of the spectra is shown expanded in the insert. The values of the parameters of the calculations are reported in Table I.

The results are satisfactory and one can observe that the frequencies of the CT bands are well reproduced: CT1 shifts to lower frequency at 0.67 eV, but the frequency of CT2 remains unchanged. The intensity of the vibronic band, over the background due to CT1 band, does not show a great variation, although its frequency is higher due to the shift of 15 cm^{-1} of the unperturbed frequency. As expected, the overall intensity of the calculated spectrum for the high pressure situation is larger (about 40%) than that calculated for the room pressure one and, according to the above considerations, the almost unchanged intensity of the vibronic band has been obtained by decreasing the dimerization of the 4S ring (see Table I).

IV. CONCLUSION

The linear optical spectra of one-dimensional charge-transfer molecular compounds are usually good and reliable experimental data and their exploitation offers the opportunity of obtaining basic information on the fundamental interactions of these type of solids. Furthermore, since the structure of these molecular compounds can be influenced by external parameters such as temperature and pressure one can easily control an important characteristic of these solids, namely the distortion of the one-dimensional dimerization.

In this paper it has been shown how the 4S-ring model, suitable for interpreting the optical data of half-filled and dimerized one-dimensional compounds, makes it possible to understand the variation of the optical data of K-TCNQ, a representative charge-transfer molecular crystal, as a function of pressure. The data were exploited considering an increase of the average value of both the charge transfer crystal $\bar{t}$ and of the intermolecular Coulomb interaction V. Also the dimerization of the stacks was influenced by pressure and the fitting of the data shows that it was strongly reduced. The fitting of the spectra confirms that the B band has to be related to the calculated CT2 charge-transfer band and, therefore, to an excitation that can be observed only for the dimerized state, as previously deduced from the temperature-dependent optical spectra.[6] However, the calculations show that the energy separation between A and B bands is not simply related to a bandwidth described as $4\bar{t}$ as previously suggested.[11] The excitation gap observable in the conductivity spectra is mainly determined by electron correlations and only in small part by the dimerization of the stacks. The pressure, up to about 5 GPa, does not induce a drastic reduction of electronic correlations and taking $(U - V)$ as the energy of the effective electronic interactions, its ratio to the bandwidth $4\bar{t}$ is 1.2 and 1.0 for the room pressure and for the 4.91 GPa situations, respectively. Therefore, electronic correlations are always of the order of the bandwidth and cannot be included in a calculation as perturbations, nor they can be considered as dominant interactions.

The study of the linear optical properties of one-dimensional compounds such as K-TCNQ, whose structure has inversion symmetry points, gives information on B_u excited states which are the only states accessible from the A_g ground state. Other interesting information would come, as in the case of polymers, from the study of the nonlinear optical properties since in this case also excited states of A_g symmetry are observable. These data are not available at present but they are of particular interest because they should display important variation as a function of the dimerization induced by temperature or pressure. Furthermore their comparison with the data available for polymers would allow one to gain information also on these latter materials.

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