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# A key to the understanding of electron–molecular vibration coupling in organic charge-transfer salts: application of the two-site Hubbard model

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**Abstract.** A two-site Hubbard model has been utilized for description of the electron–molecular vibration coupling (EMVC) in organic charge-transfer (CT) salts with dimerized structures. It was shown that the intermolecular charge oscillations in the anti-phase totally symmetric vibrations are accompanied by a decrease of energy of the occupied electronic state in the dimer. This effect is responsible for the frequency shift of i.r.-active electron-vibrational bands compared with relevant Raman modes, and can be described in terms of dimensionless coupling constants. The absorption coefficients for the bands were found to be proportional to the frequency shifts. The calculated values are in good quantitative agreement with experimental data for BEDT-TTF-based and TTF-based monovalent CT complexes.

## 1. Introduction

Optical properties of organic charge-transfer (CT) salts of different families have been the subjects of numerous studies—see [1, 2]. One common feature has been found to be characteristic for all substances with dimerized structures. Infrared spectra of compounds formed by radical molecules exhibit some additional bands which are not observed in the spectra of neutral species. The bands, called frequently electron-vibrational or ‘vibronic’ bands, reveal themselves not only in the solid state but also in concentrated solutions. They originate from Ferguson–Matsen ‘charge oscillations’ known of for isolated CT complexes [3]. In conducting complexes of mixed valency the bands are strongly broadened due to coupling with free carriers and are distinctly observed on the background of an intense electronic transition. In quasi-one-dimensional semiconducting compounds the shape of the spectrum can be described within the framework of linear response theory [4, 5]. However, a comprehensive theoretical explanation of the phenomena is lacking up to now.

The additional bands are clearly seen in i.r. spectra of monovalent insulating CT salts, particularly of the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) family [6, 8]. In these compounds the lowest electronic CT excitation is located at about 1.18 eV and is well separated from the region of molecular vibrations. It was shown that the most intense i.r. bands in the salts at 1401, 1331, 489 and 476  $\text{cm}^{-1}$  are caused by coupling of four totally symmetric Raman-active  $a_g$  vibrations  $\nu_2$ ,  $\nu_3$ ,  $\nu_9$  and  $\nu_{10}$  of the donor with charge localized on molecules [6]. They are absent in the absorption spectrum of neutral

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BEDT-TTF and reveal themselves in the salt at frequencies somewhat lower than relevant Raman transitions (1455, 1431, 511 and 489  $\text{cm}^{-1}$  correspondingly). The differences in frequencies of matching i.r. and Raman bands are equal for these vibrations to 54, 100, 22 and 13  $\text{cm}^{-1}$  respectively. Quite similar peculiarities were observed in the spectra of monovalent tetrathiafulvalene (TTF) salts [7].

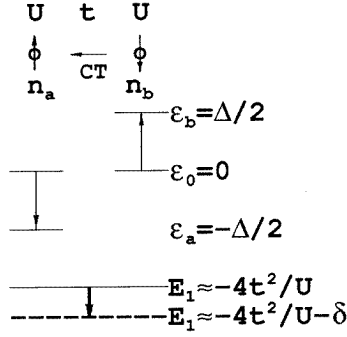
It was shown that positions of the electron-vibrational bands may be reproduced using a normal coordinate analysis of a molecular dimer [8]. The bands were treated as anti-phase vibrations ( $\nu_n^-$ ) of molecules in the dimer that appear in the spectra due to intermolecular charge transfer. Their shift relatively to matching in-phase modes ( $\nu_n^+$ ) was introduced with the help of empirical intermolecular force constants.

It is known that electron-electron correlations are crucial for analysis of low-energy electronic excitations in the monovalent salts [1]. A two-site Hubbard model is normally applied for the evaluation of the energy of the lowest CT transition in these compounds [9]. EMVC in the CT salts was considered in [4]; the solution for the dimer with two interacting electrons was obtained using the perturbation method. In the present work the coupling effect was included directly into the Hubbard model. Assuming that the intermolecular CT in the anti-phase vibrations is controlled by the electron-electron interaction in the dimer, we obtained energy shifts and relative intensities of the electron-vibrational bands. Calculated values are compared with experimental data for BEDT-TTF-based and TTF-based monovalent complexes.

## 2. Formulation

Following [4, 5] a dimer formed by two radical molecules is considered as a smallest structural unit responsible for optical properties of the substances. In agreement with [10] we suggest that the unpaired electron in each molecule resides in a nondegenerate electronic state which is well separated from other energy levels. In donor compounds the state is related to the highest occupied molecular orbital (HOMO). Motions of atoms in molecules are supposed to be correlated due to the intermolecular charge transfer controlled by the Hubbard interaction  $U$  and hopping (transfer) integral  $t$ . The molecules in the dimer may vibrate in the in-phase or the anti-phase manner. For simplicity only totally symmetric  $a_g$  intramolecular modes are taken into account. In figure 1 the molecules are approximated with two atoms located at sites a and b. Each atom bears one unpaired electron. A quite similar approach was employed in [4, 5]. However, in order to solve for a two-site Hamiltonian directly, we introduce intramolecular vibrations of molecules in a different way.

It was shown [10, 11] that displacements of atoms in totally symmetric molecular vibrations induce a shift of the energy level occupied by the unpaired electron. The deviation  $\Delta$  from an equilibrium energy  $\varepsilon_0$  in the  $n$ th vibration can be calculated by a quantum-chemical method for a single molecule. These values are usually described in terms of dimensionless coupling constants  $g_n$  [10]. They are defined as deviations of the HOMO energy with respect to the variation of a normal coordinate of the mean square amplitude for zero vibration and normalized by  $h\nu_n$ . Assuming that the vibration with energy  $\frac{1}{2}h\nu_n$  induces a HOMO shift  $\Delta_n/2$ , one can write  $g_n = \Delta_n/(2\sqrt{2}h\nu_n)$  (a further index  $n$  in  $\Delta_n$  is missed). We will search for two-electron energies and intermolecular CT in the dimer originating from the shifts of the one-electron energies  $\Delta$  and stipulated by the hopping  $t$ . Instead of separate consideration of the electronic and vibrational parts of the task (as in [4]), we will evaluate changes of the two-electron energies when atoms in molecules are



**Figure 1.** A schematic representation of a molecular dimer. Anti-phase variations of one-electron energies and the relevant shift of the lowest two-electron state of the dimer are shown with thin and thick arrows correspondingly. The notation is described in the text.

displaced from equilibrium positions in the in-phase and anti-phase modes. The vibrations of molecules are introduced using the parameter  $\Delta$ .

The Hamiltonian for the model may be written as follows:

$$H = \epsilon_a n_a + \epsilon_b n_b + t \sum_{\sigma} (a_{\sigma}^{\dagger} b_{\sigma} + b_{\sigma}^{\dagger} a_{\sigma}) + U(n_{a,+} n_{a,-} + n_{b,+} n_{b,-}) \quad (1)$$

where  $a_{\sigma}^{\dagger}$  ( $b_{\sigma}^{\dagger}$ ) and  $a_{\sigma}$  ( $b_{\sigma}$ ) denote site fermion creation and destruction operators for the unpaired electron, and  $\sigma = \pm 1$  is the electronic spin projection. As usual,  $n_{a,\sigma} = a_{\sigma}^{\dagger} a_{\sigma}$ ,  $n_{b,\sigma} = b_{\sigma}^{\dagger} b_{\sigma}$ ,  $n_a = n_{a,\sigma} + n_{a,-\sigma}$ ,  $n_b = n_{b,\sigma} + n_{b,-\sigma}$  are the electron number operators for sites a and b correspondingly.  $\epsilon_a$  and  $\epsilon_b$  are measured relatively to the equilibrium value  $\epsilon_0$  and can be equal to  $\pm\Delta/2$  if a vibration with energy  $h\nu$  is excited in the dimer (figure 1). The Hamiltonian comprising the last two terms was considered earlier by Harris and Lange [12].

It is convenient to introduce the following set of basis states for the two-electron system:

$$\begin{aligned} |u\rangle &= a_{+}^{\dagger} a_{-}^{\dagger} |0\rangle \\ |v\rangle &= b_{+}^{\dagger} b_{-}^{\dagger} |0\rangle \\ |x\rangle &= a_{+}^{\dagger} b_{-}^{\dagger} |0\rangle \\ |y\rangle &= b_{+}^{\dagger} a_{-}^{\dagger} |0\rangle. \end{aligned}$$

Then the Hamiltonian becomes the  $4 \times 4$  matrix

$$\begin{pmatrix} 2\epsilon_a + U & 0 & t & t \\ 0 & 2\epsilon_b + U & t & t \\ t & t & \epsilon_a + \epsilon_b & 0 \\ t & t & 0 & \epsilon_a + \epsilon_b \end{pmatrix}. \quad (2)$$

As usual, eigenfunctions are sought in the form

$$|E_i\rangle = \alpha_i |u\rangle + \beta_i |v\rangle + \phi_i |x\rangle + \eta_i |y\rangle. \quad (3)$$

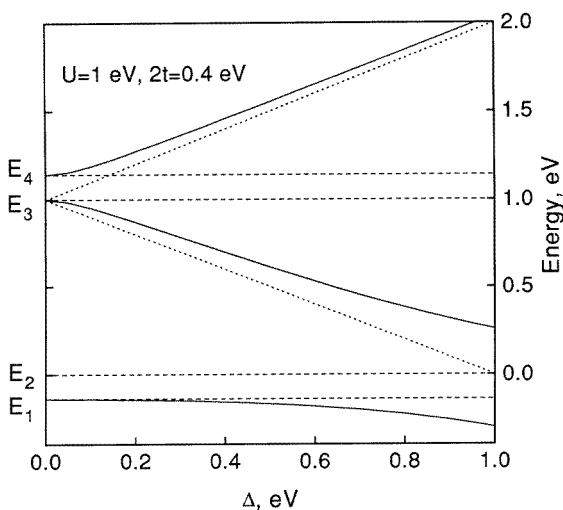
The relation  $\epsilon_a = \epsilon_b = 0$  corresponds to the conventional solution [12]. The eigenvalues calculated exactly and the magnitudes obtained in the narrow-band limit ( $t \ll U$ ) for four two-electron states are

$$\begin{aligned} E_4 &= U/2 + \sqrt{(U/2)^2 + 4t^2} \simeq U + 4t^2/U \\ E_3 &= U \\ E_2 &= 0 \\ E_1 &= U/2 - \sqrt{(U/2)^2 + 4t^2} \simeq -4t^2/U. \end{aligned} \quad (4)$$

The coefficients in equation (3) become equal to

$$\begin{aligned} \alpha_3 &= -\beta_3 = 1/\sqrt{2} & \phi_3 &= \eta_3 = 0 \\ \alpha_2 &= \beta_2 = 0 & \phi_2 &= -\eta_2 = 1/\sqrt{2} \\ \alpha_i &= \beta_i = \frac{E_i/2t}{\sqrt{2}\sqrt{1+(E_i/2t)^2}} & \phi_i &= \eta_i = \frac{1}{\sqrt{2}\sqrt{1+(E_i/2t)^2}} \quad i = 1, 4. \end{aligned} \quad (5)$$

The level diagram for the dimer is shown in figure 2 with dashed lines ( $U = 1$  eV,  $2t = 0.4$  eV). The sum of four energies is  $\sum_{E_i} = 2U$  (a trace of the matrix (2)).



**Figure 2.** The dependence of energies for four two-electron states of the dimer on the difference of one-electron energies  $\Delta$  (solid lines). The cases where  $\Delta = 0$ ,  $t \neq 0$  and  $\Delta \neq 0$ ,  $t = 0$  are shown with dashed and dotted lines respectively.

Optical excitations are allowed between states for which the matrix element of the transition dipole moment

$$\langle E_i | n_a - n_b | E_j \rangle = 2(\alpha_i \alpha_j - \beta_i \beta_j) \quad (6)$$

has a nonzero magnitude. From the lowest energy state the allowed CT transition is only to the state with energy  $U$  (see also [4]):

$$E_{CT} = U/2 + \sqrt{(U/2)^2 + 4t^2}. \quad (7)$$

We can estimate also magnitudes of matrix elements related to the occupation of sites and electron hopping. For  $i$ th state they are expressed correspondingly as

$$\begin{aligned} \langle E_i | a_+^\dagger a_+ + a_-^\dagger a_- + b_+^\dagger b_+ + b_-^\dagger b_- | E_i \rangle &= 2(\alpha_i^2 + \beta_i^2) \\ \langle E_i | a_+^\dagger b_+ + a_-^\dagger b_- + b_+^\dagger a_+ + b_-^\dagger a_- | E_i \rangle &= 2(\phi_i^2 + \eta_i^2). \end{aligned} \quad (8)$$

In the narrow-band limit for the lowest energy state we obtain

$$\alpha_1^2 + \beta_1^2 = \frac{4t^2}{U^2 + 4t^2} \quad \phi_1^2 + \eta_1^2 = \frac{U^2}{U^2 + 4t^2}. \quad (9)$$

Equations (4) and (9) show that an increase of the hopping  $t$  causes the increase of the occupation of the sites and decrease of the energy  $E_1$ .

Due to intramolecular vibrations, one-electron energies in the dimer may vary, and a more general form of the Hamiltonian (2) has to be considered. In the in-phase vibrations

the energy shifts are  $\varepsilon_a = \varepsilon_b = \Delta/2$  and the eigenvalues of the Hamiltonian become equal to

$$\begin{aligned} E_4 &= \Delta + U/2 + \sqrt{(U/2)^2 + 4t^2} \\ E_3 &= \Delta + U \\ E_2 &= \Delta \\ E_1 &= \Delta + U/2 - \sqrt{(U/2)^2 + 4t^2}. \end{aligned} \quad (10)$$

One can see that the energy spectrum of the dimer is the same as earlier (equation (4)); its origin only shifts by  $\Delta$ . The excitation of the in-phase vibration  $\nu^+$  in the dimer contributes to its energy as

$$E_a^{el}/2 + E_b^{el}/2 + |\Delta/2| + |\Delta/2| = E^{el} + \Delta = h\nu$$

where  $E^{el}$  is a variation of an elastic energy of the molecule taken in addition to the change of its electronic term  $\Delta$ . Obviously the in-phase mode has the same energy as the corresponding vibration of a single molecule  $h\nu$  and therefore is completely decoupled from the electronic system of the dimer.

In anti-phase vibrations the deviations of one-electron energies have opposite signs,  $\varepsilon_b = -\varepsilon_a = \Delta/2$  (figure 1). The eigenvalues of the Hamiltonian (2) can be found as roots of following algebraic equation:

$$E(E^3 - 2UE^2 + (U^2 - 4t^2 - \Delta^2)E + 4t^2U) = 0. \quad (11)$$

Analytical solution of the equation leads to cumbersome expressions for all roots with the evident exception of  $E_2 = 0$ . That is why we carried out the numerical evaluation. The level diagram obtained as a function of the difference of one-electron energies  $\Delta$  is shown in figure 2 with solid lines. Evidently the shape of the spectrum changes. As earlier,  $\sum E_i = 2U$ .

One can easily calculate the variation of two-electron energies induced by  $\Delta$  in the system when no hopping is allowed. The eigenvalues for  $t = 0$ ,  $E_4 = U + \Delta$ ,  $E_3 = U - \Delta$ ,  $E_2 = E_1 = 0$ , are shown in figure 2 with dotted lines. Two lowest energy levels are independent of  $\Delta$  (as a sum of the same one-electron values with opposite signs) and in the two highest energy states the shift of the one-electron energies is just doubled because two electrons occupy the same site. Obviously if  $t = 0$  the anti-phase mode  $\nu^-$  has the same energy as the relevant vibration of a single molecule,

$$E_a^{el}/2 + E_b^{el}/2 + |-\Delta/2| + |\Delta/2| = E^{el} + \Delta = h\nu.$$

The solution for  $t \neq 0$  can be obtained in the narrow-band limit. The case where  $t, \Delta \ll U$  is normally observed in real organic compounds. Expansion of the roots of equation (11) near  $U + 4t^2/U + \Delta$ ,  $U - \Delta$  and  $-4t^2/U$  gives the following expressions:

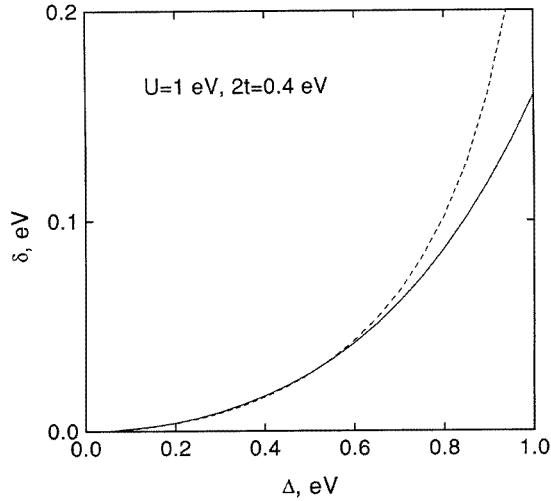
$$\begin{aligned} E_4 &= U + \Delta + \frac{4t^2}{U} \left[ 1 - \frac{\Delta(U + 2\Delta)}{4t^2 + 2\Delta(U + \Delta)} \right] \\ E_3 &= U - \Delta \left[ 1 - \frac{4t^2}{4t^2 + 2\Delta(U - \Delta)} \right] \\ E_2 &= 0 \\ E_1 &= -\frac{4t^2}{U} \left[ 1 + \frac{\Delta^2(U^2 - 4t^2)}{U^2(U^2 + 12t^2 - \Delta^2)} \right]. \end{aligned} \quad (12)$$

Due to the linearization used,  $\sum E_i$  is not exactly  $2U$  as was observed for the numerical solution.

The lowest energy state is the most important for us. This is the highest electronic state in the dimer occupied by electrons and the only occupied state which contributes to its electronic energy within the framework of our model. Energy variations of occupied states are responsible for frequencies of molecular vibrations [13]. One can see that the energy of the state now depends on  $\Delta$ . Its deviation  $\delta$  from the constant value  $-4t^2/U$  is equal to

$$\delta = \frac{4t^2}{U} \frac{\Delta^2(U^2 - 4t^2)}{U^2(U^2 + 12t^2 - \Delta^2)}. \quad (13)$$

Figure 3 shows that equation (13) approximates the numerical solution very well even at quite big  $\Delta$ .



**Figure 3.** The deviation of the energy of the lowest two-electron state of the dimer  $\delta$  versus the difference of one-electron energies  $\Delta$  calculated from equation (13) (dashed line) and obtained by numerical evaluation of equation (11) (solid line).

The energy of the anti-phase vibration  $\nu^-$  can be written as

$$E_a^{el}/2 + E_b^{el}/2 + |-\Delta/2| + |\Delta/2| - \delta = E^{el} + \Delta - \delta = h\nu - \delta.$$

Compared with that of the single molecule or in-phase dimeric mode, the energy decreases due to the appearance of the electron-vibrational term  $\delta$ . The anti-phase mode couples with the electronic system of the dimer and should reveal itself in the spectrum with the energy shift  $\delta$ .

The expressions for the coefficients of the eigenfunctions are

$$\begin{aligned} \alpha_2 &= \beta_2 = 0 & \phi_2 &= -\eta_2 = 1/\sqrt{2} \\ \alpha_i &= \frac{U - E_i + \Delta}{D} & \beta_i &= \frac{U - E_i - \Delta}{D} \\ \phi_i &= \eta_i = \frac{2t}{E_i} \frac{U - E_i}{D} & i &= 1, 3, 4 \end{aligned} \quad (14)$$

$$D = \sqrt{2} \sqrt{\left(1 + \frac{4t^2}{E_i^2}\right) (U - E_i)^2 + \Delta^2}.$$

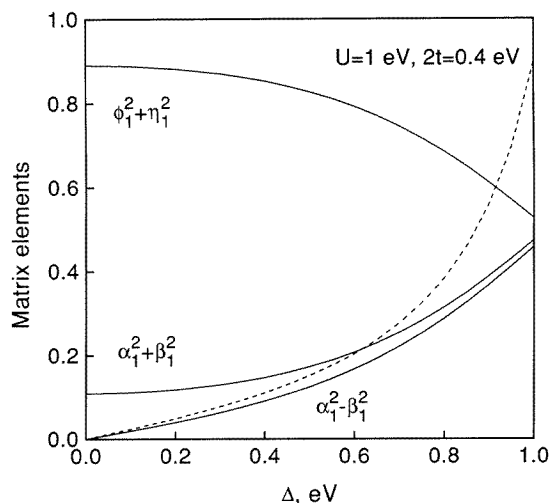
As long as  $\alpha_i \neq \beta_i$  ( $i = 1, 3, 4$ ) the occupation of the sites is not the same, and the difference  $n_a - n_b = \langle E_i | n_a - n_b | E_i \rangle = 2(\alpha_i^2 - \beta_i^2)$  may be immediately evaluated:

$$\alpha_i^2 - \beta_i^2 = \frac{4\Delta(U - E_i)}{D^2} \quad i = 1, 3, 4. \quad (15)$$

For the lowest energy state in the narrow-band limit and  $\Delta \ll t$  we obtain

$$\alpha_1^2 - \beta_1^2 = 2\Delta \frac{4t^2 U}{(U^2 + 4t^2)^2}. \quad (16)$$

The magnitudes of the matrix elements defined according to equation (8) were calculated numerically and for the lowest energy state are shown in figure 4 as a function of  $\Delta$ . One can see that an increase of  $\Delta$  causes the increase of  $\alpha_1^2 + \beta_1^2$  and equal decrease of  $\phi_1^2 + \eta_1^2$ . A quite similar rise in the occupation of the sites can be induced in the dimer by increasing the hopping  $t$ , equation (9), and is also accompanied by a decrease of the energy  $E_1$ , equation (4). So the influence of  $\Delta$  on the electronic system of the dimer has quite a similar nature and provokes an energy shift  $\delta$  of the lowest energy state. The occupation of the sites now increases due to the intermolecular CT in anti-phase vibrations.



**Figure 4.** The matrix elements for the lowest two-electron state of the dimer versus the difference of one-electron energies  $\Delta$  calculated from equation (16) (dashed line) and obtained by numerical evaluation of equations (11) and (14) (solid lines).

It is known that the absorption coefficient of an i.r. band is proportional to the square of the matrix element of the transition dipole moment [13]. We have shown earlier that due to the lack of intermolecular charge transfer, the situation with completely decoupled in-phase vibrations is equivalent to the case of isolated molecules, when in particular  $\alpha_i = \beta_i$ . Therefore the matrix element of the transition dipole moment between states with and without (marked with an asterisk) the anti-phase vibration can be written as

$$\langle E_1 | n_a - n_b | E_1^* \rangle = 2(\alpha_1 \alpha_1^* - \beta_1 \beta_1^*) = 2\alpha_1^*(\alpha_1 - \beta_1).$$

This magnitude is evidently proportional to

$$n_a - n_b = 2(\alpha_1 + \beta_1)(\alpha_1 - \beta_1)$$

( $\alpha_1 + \beta_1 \approx \text{constant}$ ; see equation (14)), i.e., the intermolecular CT provoked by  $\Delta$ . In the limit where  $\Delta \ll t$  the square of the latter difference can easily be evaluated from equation (14) and equation (13):

$$(\alpha_1 - \beta_1)^2 = \delta \frac{2U^5(U^2 + 12t^2)}{(U^2 + 4t^2)^3(U^2 - 4t^2)}. \quad (17)$$

One can see a linear dependence of the absorption caused by CT in the anti-phase vibration on the energy shift  $\delta$ . This is the consequence of their common origin in the intermolecular charge oscillation.



### 3. Discussion and comparison with experiment

The CT in anti-phase vibrations with nonzero  $\Delta$  is accompanied by a shift  $\delta$  of the occupied energy level of the dimer. The ‘vibronic’ shift is not observed if  $t = 0$  and in the in-phase modes. The influence of  $\Delta$  on the electronic system of the dimer is quite similar in nature to the variation of occupation of the sites caused by the increase of the hopping  $t$ . In the classical approach the decrease of energy of the ground state of the dimer due to coupling with anti-phase vibrations can be introduced with the help of intermolecular force constants [8], i.e., second derivatives of the energy with respect to changes of the molecular-vibrational coordinates [13]. The intermolecular CT in the anti-phase vibrations reveals itself as a decrease of stiffness of the molecules.

The intermolecular CT results in the appearance of intense bands in i.r. spectra. The unusual electron-vibrational bands are definitely observed in the spectroscopic experiment [6, 7]. The term linear in  $\Delta$  in equation (16) for the difference  $n_a - n_b$  is relevant to the shift of one-electron energies in the dimer and reveals itself for any  $\Delta$  inserted in the Hamiltonian (2). The absorption coefficient for the i.r. bands provoked by anti-phase vibrations is proportional to the energy shift  $\delta$ . The latter is equal to the frequency shift  $S$  between matching i.r. and Raman modes.

It should be mentioned that for small  $\Delta$  the precise anti-phase relation required for the one-electron energies in the dimer may be easily destroyed by temperature fluctuations of charge carriers in the compound. This should cause an abrupt decrease of intensities of the electron-vibrational bands in the limit  $\Delta \rightarrow 0$  which is not predicted by our simple model.

**Table 1.** Experimental and calculated relative intensities and dimensionless coupling constants  $g_n$  for electron-vibrational bands in BEDT-TTF-based [6] and TTF-based [7, 14] monovalent CT salts. The frequencies are in  $\text{cm}^{-1}$ .

$n$	$\nu_n^+$ (observed)	$\nu_n^-$ (observed)	$S_n$ (observed)	$I_n/I_3$ (observed)	$I_n/I_3$ (calculated)	$g_n^\dagger$ (calculated)	$g_n^\ddagger$ (calculated)
BEDT-TTF							
2	1455	1401	54	0.814	0.798	0.165	0.564
3	1431	1331	100	1.000	1.000	0.746	0.763
9	511	489	22	0.495	0.450	0.476	1.041
10	489	476	13	0.216	0.294	0.050	0.840
TTF							
2	1506	1503	3	0.088	0.043	0.23	0.148
3	1430	1360	70	1.000	1.000	0.62	0.734
5	758	749	9	0.118	0.129	0.49	0.507
6	510	492	18	0.265	0.257	1.33	1.063

$\dagger$  Calculated by a quantum-chemical method for single BEDT-TTF [6] and TTF [10] molecules.

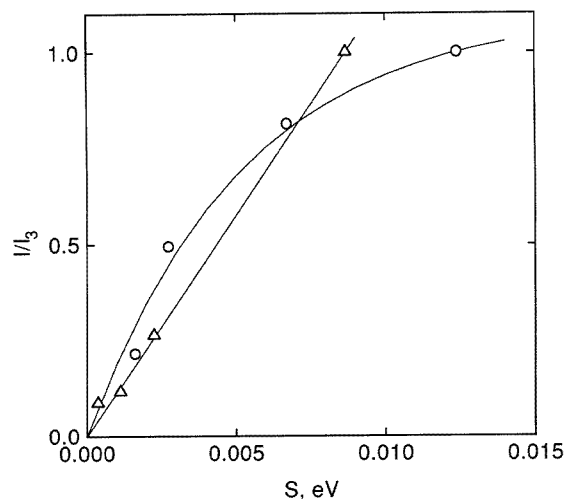
$\ddagger$  Defined as  $g_n = \Delta_n / (2\sqrt{2}h\nu_n)$  for  $\Delta_n$  calculated on the basis of equation (13),  $\delta_n = S_n$ .  $t = 0.19$  eV,  $U = 1.06$  eV and  $t = 0.27$  eV,  $U = 1.42$  eV for BEDT-TTF-based and TTF-based salts respectively.

The comparison with experiment was performed using data on the BEDT-TTF-based [6] and TTF-based [7, 14] monovalent CT salts mentioned in the introduction. Frequencies of electron-vibrational bands ( $\nu_n^-$ ), their relative intensities  $I_n/I_3$  (measured as absorbance and normalized with the intensity of the strongest band) as well as frequency shifts  $S_n = \nu_n^+ - \nu_n^-$  compared with matching Raman-active modes ( $\nu_n^+$ ) are collected together in table 1 and are shown in figure 5. The intensities were also evaluated on the assumption that the absorption coefficient for the bands  $A(\nu)$  depends linearly on their shifts  $S(\nu)$ , i.e.,  $A(\nu) = c_1 S(\nu)$ ,

where  $c_1$  is a constant. According to the Lambert–Beer law we have

$$I(\nu) = 1 - \exp[-c_2 A(\nu)] \quad (18)$$

where  $c_2$  is a scale factor. In the case of a weak absorption  $c_2 A(\nu) \ll 1$ , equation (18) can be simplified to  $I(\nu) = c_2 A(\nu)$ . The i.r. spectra of BEDT-TTF-based and TTF-based salts were measured on a KBr pellet and on  $0.23 \text{ mol dm}^{-3}$  of solution in dimethylsulphoxide correspondingly. Results of the mean square fitting of the relative value  $I/I_3$  to the experimental data are shown in figure 5. It appears that the powder spectrum is described very well by equation (18) ( $c_1 c_2 = 192$ ) whereas the solution data are in excellent agreement with the linear dependence  $I(\nu) \sim S(\nu)$  and both exhibit the same trends.



**Figure 5.** Relative intensities of electron-vibrational bands  $I_n/I_3$  versus the energy shift  $S$  for BEDT-TTF-based (circles) and TTF-based (triangles) monovalent CT salts obtained experimentally [6, 7] and evaluated using equation (18),  $A(\nu) \sim S(\nu)$  and  $I(\nu) \sim S(\nu)$  (solid lines for both compounds respectively).

Using experimental values of  $S_n$  we estimated values of  $\Delta_n$  using equation (13). These are shown in table 1 as dimensionless coupling constants  $g_n = \Delta_n / (2\sqrt{2}h\nu_n^+)$ . The transfer integral  $t$  was taken as equal to 0.19 eV (reported in [15]), and  $U = 1.06$  eV (evaluated from equation (7) using  $E_{CT} = 1.18$  eV [6]) for BEDT-TTF-based salts; and  $t = 0.27$  eV [9],  $U = 1.42$  eV and  $E_{CT} = 1.6$  eV [7] for TTF-based salts. The values obtained can be compared with  $g_n$  calculated by a quantum-chemical method for single BEDT-TTF [6] and TTF [10] molecules (see table 1). Very similar  $g_n$ -values were also reported in [16]. The agreement with magnitudes obtained in our simple two-site approximation is quite good for high-frequency  $\nu_2$ - and  $\nu_3$ -vibrations (C=C stretchings). The  $g_n$ -values evaluated by us for low-frequency modes (C–S stretchings in the central fragments of molecules) are higher than those reported for  $\nu_9$ - and  $\nu_{10}$ -vibrations in BEDT-TTF [6] but approach the values for analogous  $\nu_5$ - and  $\nu_6$ -vibrations in smaller TTF molecules [10]. One can speculate that some differences in both sets of  $g_n$  are caused by a competition of the intramolecular [6] and intermolecular CT. The latter should slightly change the forms of intramolecular vibrations and can therefore influence  $\Delta$ . It seems that the competition is stronger in ‘spacious’ molecules and mainly affects less characteristic low-frequency modes.

In conclusion, the variation of one-electron energies in molecular vibrations has been included into the two-site dimer model with Hubbard interaction. It was shown that the intermolecular CT in anti-phase vibrations is accompanied by a decrease of energy of the occupied two-electron state of the dimer. The effect is responsible for the frequency shift of the electron-vibrational bands observed in i.r. spectra of organic CT salts with dimerized

structures. The absorption coefficients of the bands are proportional to the frequency shifts. The calculated values are in good quantitative agreement with experimental data on BEDT-TTF-based and TTF-based monovalent CT complexes.

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### References

- [1] Jacobsen C S 1988 Optical properties *Semiconductors and Semimetals* vol 27, ed E Conwell (San Diego, CA: Academic) p 293
- [2] Williams J M, Ferraro J R, Thorn R J, Carlson K D, Geiser U, Wang H H, Kini A M and Whangbo M-H 1992 *Organic Superconductors (Including Fullerenes)* (Englewood Cliffs, NJ: Prentice-Hall)
- [3] Ferguson E E and Matsen F A 1958 *J. Chem. Phys.* **29** 105
- [4] Rice M J 1979 *Solid State Commun.* **31** 93
- [5] Rice M J, Yartsev V M and Jacobsen C S 1980 *Phys. Rev. B* **21** 3437
- [6] Kozlov M E, Pokhodnia K I and Yurchenko A A 1989 *Spectrochim. Acta A* **45** 437
- [7] Bozio R, Zanon I, Girlando A and Pecile C 1979 *J. Chem. Phys.* **71** 2282
- [8] Kozlov M E and Tokumoto M 1994 *Spectrochim. Acta A* **50** 2271
- [9] Torrance J B, Scott B A, Welber B, Kaufman F B and Seiden P E 1979 *Phys. Rev. B* **19** 730
- [10] Lipari N O, Rice M J, Duke C B, Bozio R, Girlando A and Pecile C 1977 *Int. J. Quantum Chem.* **11** 583
- [11] Lipari N O, Duke C B and Pietronero L 1976 *J. Chem. Phys.* **65** 1165
- [12] Harris A B and Lange R V 1967 *Phys. Rev.* **157** 295
- [13] Gribov L A and Orville-Thomas W J 1988 *Theory and Methods of Calculation of Molecular Spectra* (New York: Wiley)
- [14] Painelli A, Girlando A and Pecile C 1984 *Solid State Commun.* **52** 801
- [15] Jacobsen C S, Tanner D B, Williams J M, Geiser U and Wang H H 1987 *Phys. Rev. B* **35** 9605
- [16] Faulhaber J C R, Ko D Y K and Briddon P R 1993 *Synth. Met.* **60** 227