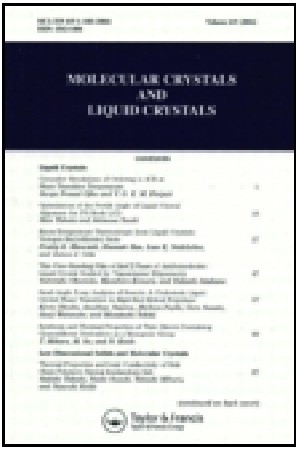

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Electron-Phonon Coupling in Low Dimensional Organic Superconductors

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ELECTRON–PHONON COUPLING IN LOW DIMENSIONAL ORGANIC SUPERCONDUCTORS

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Abstract The relative importance of the coupling of electrons with intra– and inter–molecular phonons in setting up the organic superconductivity is addressed. We base our considerations on a firmly established set of electron molecular vibration coupling constants for the TMTTF molecule. By the use of three different models of the BCS, strong coupling and non adiabatic type we find that, in order to attain critical temperatures (T_c) in the typical range of 1 to 10 K, large values for the electron inter–molecular phonon coupling constants are needed. We also report a theoretical analysis of the effects of isotopic substitution of the carbon atoms in a TTF based molecule. Through a simple model of two coupled oscillators and by the use of the experimental data available for TMTTF, we estimate isotopic T_c shifts which may be useful for qualitative comparison with experimental data.

INTRODUCTION

In this paper we discuss some aspects of the electron–phonon (EP) coupling effects in low–dimensional (LD) organic superconductors like the well known Bechgaard salts and the (BEDT–TTF)$_2$X compounds.[1,2] These materials are built up from large planar molecules derived from the TTF structure (TTF = tetrathiafulvalene). This gives a sort of uniformity to the molecular (electronic and vibrational) properties of these compounds. The role of the electron–phonon coupling in the setting up of superconductivity in LD organic materials is still debated.[1,2] It is well known that in organic superconductors, as in all the conducting molecular materials, there are essentially two types of interaction of the conduction electrons with the phonons. One involves the internal molecular vibrations that are characteristic of the organic molecular structure. The other involves the intermolecular phonons consisting of approximately rigid motions of the molecules around their equilibrium position and orientation in the crystal lattice.

Very recent results[3] obtained for the β_H phase of (BEDT–TTF)$_2$I$_3$ by isotopic substitution of the two carbon atoms in the central double bond of BEDT–TTF have shown a strong isotopic effect on the superconducting critical temperature (T_c). The very large amplitude of the T_c shift ($\simeq -7.5\%$) was taken as an indication of a strong role of the intramolecular vibrations in these organic superconductors.

On the other hand the same type of experiment[4] carried out on the κ-phases of $(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ and $(BEDT\text{-}TTF)_2Cu(NCS)_2$ showed no detectable isotopic effect on T_c within an experimental error of about 1%. This result, together with extensive and accurate structural studies[5] that correlate the pressure and anion dependence of T_c in BEDT-TTF based superconductors to their crystal lattice softness, suggest an important role of the coupling with intermolecular phonons in organic superconductivity.

In the first and second section of this work we point the attention to the role of the electron-phonon coupling in organic superconductivity summarizing the present knowledge of the relevant interaction parameters. In an attempt at assessing the relative importance of intra- and intermolecular vibrations in mediating superconductivity in TTF based materials we make use of a set of well established experimental data regarding the electronic structure and the vibronic interactions in some representative $(TMTSF)_2X$ and $(TMTTF)_2X$ compounds[6,7] to calculate the critical temperature according to three different models[8-10] for phonon driven superconductivity in molecular materials.

In the third section we present an analysis of the effects of isotopic substitution of the carbon atoms in the central and external double bonds of a TTF based molecule. Through a simple model of two coupled oscillators and by the use of the experimental data available for TMTTF,[11,7] we calculate the isotopic T_c shifts predicted by the three above mentioned models for proper comparison with the reported experimental data.

ELECTRON-PHONON COUPLING

Electron molecular vibration coupling

In the organic superconductors there are essentially two types of interactions of the conduction electrons with phonons. The more extensively studied mechanism, on which well established experimental information is available, is the coupling with the internal totally symmetric (a_g) molecular vibrations[12] that modulate the energy of the conduction electron molecular orbital (HOMO). The linear electron-molecular vibration (EMV) coupling constant g_i for each ith coupled mode is defined as the derivative of the HOMO energy, ϵ_{HOMO}, with respect to the ith dimensionless intramolecular normal coordinate Q_i,

$$g_i = \left(\frac{\partial \epsilon_{HOMO}}{\partial Q_i}\right)_o . \tag{1}$$

The derivative is calculated at the equilibrium geometry of the molecule.

In TTF[13] and the related TMTTF[11,7] and BEDT-TTF[14,15] molecules the vibrational modes that have the strongest coupling constants are those involving the central atoms (two carbon and four sulfur atoms) where most of the charge distribution of the HOMO is concentrated.[13,16] For TTF these modes are the ν_3 one which stretches the C=C bonds and the ν_6 mode which stretches the bonds between the central carbon and the adjacent sulfur atoms.[13]

By their definition, the EMV coupling constants can be considered, to a good level of approximation, as molecular properties that are transferable from crystal to crystal. The HOMOs in the TTF derivatives, such as TMTTF and BEDT–TTF, are very similar to that of TTF.[13,16] In fact the charge distribution is concentrated near the center of the molecules. These molecules have similar C=C and C–S stretching a_g–modes with almost the same values of the quantum energies $\hbar\omega_i$. Therefore one expects very similar EMV coupling constants in organic conductors composed of TTF related molecules.

In the last few years we have completed an analysis of the room temperature optical data of a series of $(TMTSF)_2X$ and $(TMTTF)_2X$ salts.[6,7] The data have been analysed by the use of an one–dimensional (1D) model[17] for a dimerized molecular chain where the electronic system is coupled with an arbitrary number of intramolecular modes of vibration and with an effective intermolecular mode. Beside the estimates of the electronic parameters, the analysis has allowed us to evaluate two sets of reliable EMV coupling constants for TMTSF and TMTTF.[7] The values obtained for the latter compound are reported in Table I.

TABLE I Linear EMV coupling constants for TMTTF.

a_g mode	ν_3	ν_4	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}
ω_i (cm^{-1})	1603	1478	1098	938	563	508	288	222
g_i (eV)	0.03	0.12	0.03	0.03	0.02	0.06	0.01	0.01

Electron intermolecular phonon coupling

The intermolecular modes imply oscillations of the molecules, as rigid bodies, around their equilibrium position and orientation in the crystal. During these oscillations the charge transfer integral t between nearest neighbour molecules is modulated and this is the source of the electron–intermolecular phonon (EIP) coupling.[12] The linear EIP coupling constant g_e is defined as the derivative of the charge transfer integral with respect to the dimensional intermolecular coordinate u_e ,

$$g_e = \left(\frac{\partial t}{\partial u_e}\right)_o , \qquad (2)$$

calculated with the molecules in their equilibrium position.

The knowledge concerning the EIP coupling is very poor. This is principally due to the fact that both the frequencies and the coupling constants of the intermolecular modes are strongly dependent on the crystal structures. This opposes to the transferability of the experimental data from one structure to another. Only few data on the frequencies and the coupling constants of the intermolecular modes are available. From Raman[18] and infrared[19] measurements it turns out that for the $(TMTSF)_2X$ compounds the intermolecular frequencies are centered around 50 cm^{-1}. Semiempirical quantum chemical calculations[20] indicate that for $(TMTSF)_2PF_6$ the EIP coupling constants are in the range of 0.20 to 0.35 eV Å^{-1}.

The dimerized molecular chain model we have used for analysing the optical data of $(TMTSF)_2X$ and $(TMTTF)_2X$ compounds accounts for the coupling of the electronic system with one effective intermolecular mode. The related EIP coupling constant can be estimated indirectly from a self-consistent relation between this constant and other electronic and structural parameters of the material.[17] However this estimate is strongly dependent on the values assumed for the intermolecular mode frequency. From our fit of the optical data[6,7] we obtain values for the EIP coupling constant in the range of 0.05 to 0.15 eVÅ^{-1} for $\omega_e = 50$ cm^{-1} and in the range from 0.20 to 0.60 eVÅ^{-1} for $\omega_e = 100$ cm^{-1}.

CRITICAL TEMPERATURE CALCULATIONS

Using the available experimental data, we now try to gain some hints on the relative importance of the two types of electron–phonon interactions in organic superconductors.

Our first approach is to use the model proposed by Yamaji[8] for the calculation of the critical temperature. This model is essentially based on the BCS theory but in addition, it takes into account the attractive interactions mediated by several high frequency internal molecular vibrations. It also accounts for the interaction with one low frequency intermolecular phonon and for the on-site Coulomb interaction U that opposes to the pairing. Yamaji's expression for T$_c$ is

$$k_B T_c = 1.13\,\hbar\omega_1 \exp\left[-\cfrac{1}{\lambda_1 - \cfrac{1}{x_2 - \cfrac{1}{\lambda_2 - \cfrac{1}{x_3 - \cfrac{1}{\cfrac{\cdots}{x_\nu - 1/\lambda_\nu}}}}}}\right], \qquad (5)$$

where k_B is the Boltzmann constant and

$$x_i = \frac{1}{2} \ln \left\{ \frac{\min(\hbar\omega_i, \mathrm{D}_1) \cdot \min(\hbar\omega_i, \mathrm{D}_2)}{\min(\hbar\omega_{i-1}, \mathrm{D}_1) \cdot \min(\hbar\omega_{i-1}, \mathrm{D}_2)} \right\} \qquad (6)$$

In Eq. (6) D_1 and D_2 represent the linearized bandwidths below and above the Fermi level, respectively. ω_i and λ_i are the frequencies and the dimensionless coupling constants of the coupled modes. For the lowest frequency intermolecular coupled mode

$$\lambda_1 = \lambda_e = \frac{N_F}{N} \cdot 2 \left\langle \frac{g_e^2}{\hbar\omega_e} \right\rangle_{F.S.}, \qquad (7)$$

and for the $v = \nu - 2$ intermolecular a_g coupled modes

$$\lambda_i = \frac{N_F}{N} \cdot 2\, \frac{g_i^2}{\hbar\omega_i} \qquad i = 2, .., \nu - 1 \qquad (\nu = v + 2). \qquad (8)$$

N and N_F represent the density of molecules and the density of states per spin at the Fermi level, respectively. In Eq. (7) $\langle\ \rangle_{F.S.}$ indicates an average over the Fermi surface. For our 1D chain model[17] Eq. (7) becomes

$$\lambda_e = \frac{N_F}{N} \cdot \frac{8}{M\omega_e^2} \cdot \left(\frac{\partial t}{\partial u_e}\right)_\circ^2 \qquad (9).$$

The on–site Coulomb interaction appears into Eq. (5) through $\lambda_\nu = -N_F \cdot U/N = -\mu$ and $\omega_\nu = \infty$, the opposing contribution to the pairing of the bare Coulomb potential is however screened by the retardation effect[21] (cf. Eq. (13) below).

Being confident in the transferability of the molecular parameters from TMTTF to BEDT–TTF, we use our set of TMTTF frequencies and EMV coupling constants of Table I to calculate, through Yamaji's relation, critical temperatures in the range characteristic of BEDT–TTF based superconductors, i.e. between 1 and 10 K. The principal sources of uncertainties in the present calculation are the estimates of the Coulomb repulsion energy and of the density of states at the Fermi level. To make the calculation internally consistent, we stick to the values derived from our analyses of the $(TMTTF)_2X$ salts. For the on–site Coulomb energy we use the value of 0.60 eV estimated through a cluster analysis of the low temperature infrared data of $(TMTSF)_2ReO_4$.[7] The bandwidth and the 1D density of states are derived from an effective transfer integral t of 0.20 eV. The value of $N_F = 1.13$ states per molecule obtained in this way is not very far from that estimated from 2D band calculations for a series of superconducting ET salts.[5,2]

With this set of input parameters, in order to have critical temperatures in the range of 1 to 10 K we need values for the dimensionless EIP coupling constant λ_e that range from 0.25 to 0.50 for $\omega_e = 50$ cm^{-1} or from 0.22 to 0.38 for $\omega_e = 100$ cm^{-1}. The corresponding values of the dimensional coupling constant, obtained using Eq. (9), are between 0.26 and 0.36 eVÅ^{-1} for $\omega_e = 50$ cm^{-1}, or between 0.48 and 0.64 eVÅ^{-1} for $\omega_e = 100$ cm^{-1}. They are in general larger than the values obtained from the optical data of $(TMTSF)_2X$ and $(TMTTF\ )_2X$ salts and are quite large in respect to the weak coupling requirement of BCS theory. This indicates the opportunity to explore strong coupling models.

We have considered the McMillan strong coupling relation[9,22]

$$k_B T_c = \frac{\hbar\omega_o}{1.2} \exp\left\{-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right\}, \tag{10}$$

and a new expression recently proposed by Pietronero and Strässler (hereafter PS)[10] that includes non adiabatic effects

$$k_B T_c = \frac{1.13}{\sqrt{2}} \left(\frac{1}{1+2\hbar\omega_o/E}\right) \hbar\omega_o \exp\left\{-\frac{1+\lambda/(1+2\hbar\omega_o/E)}{\lambda\cdot(1+\lambda\cdot 6\hbar\omega_o/E) - \mu^*(1+0.6\cdot\lambda)}\right\}. \tag{11}$$

In both equations λ represents the dimensionless phonon coupling constant defined through the Eliashberg function $\alpha^2(\omega)F(\omega)$ by integration over the whole phonon spectrum

$$\lambda = 2\int_0^\infty \frac{\alpha^2(\omega)F(\omega)}{\omega} d\omega, \tag{12}$$

ω_o is a characteristic phonon frequency, and μ^* is the screened Coulomb potential[1,22]

$$\mu^* = \frac{\mu}{1+\mu\cdot\ln(E/\hbar\omega_o)}. \tag{13}$$

In Eqs. (11) and (13) E represents the total bandwidth.

The McMillan expression for T_c is obtained on the basis of Migdal–Eliashberg theory of superconductivity that is strongly based on the adiabatic limit where the energy of the characteristic phonon is much less than the Fermi energy. PS have considered the situation in which this approximation breaks down including non adiabatic effects into the theory. When the ratio between the phonon and the Fermi energies is appreciably different from zero one obtains a strong enhancement of T_c.[10]

A comparison between three sets of T_c calculations done by the Yamaji, McMillan and PS expressions is shown in Figure 1. The calculations have been carried out with the values of the molecular and band parameters given above. The frequency of the coupled intermolecular mode has been kept fixed at 50 cm^{-1}. For the two strong coupling T_c equations the phonon coupling constant λ and the characteristic phonon frequency ω_o have been calculated through a discrete Eliashberg function

$$\alpha^2(\omega)F(\omega) = \frac{N_F}{N}\frac{1}{\hbar}\left\{g_e^2\delta(\omega_e-\omega)+\sum_{i=1}^{v} g_i^2\delta(\omega_i-\omega)\right\}. \qquad (14)$$

For the characteristic frequency we have chosen to use a logarithmic weight of all the phonon frequencies[22]

$$\omega_o = \omega_{ln} = \exp\left\{\frac{1}{\lambda}\left[\lambda_e \ln(\omega_e)+\sum_{i=1}^{v}\lambda_i \ln(\omega_i)\right]\right\}. \qquad (15)$$

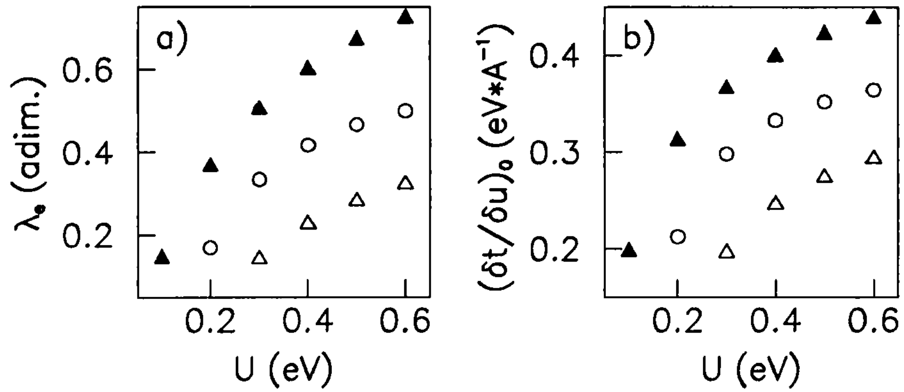

FIGURE 1 Values of the EIP coupling parameters, λ_e (a) and g_e (b), required to give T_c=10 K with the Yamaji (○), McMillan (▲) and PS (△) models.

The left panel of Figure 1 shows which values of the dimensionless EIP coupling constant are required to give a critical temperature of 10 K with an on-site Coulomb potential ranging from 0.20 to 0.60 eV. The right panel reports the corresponding values of the dimensional EIP coupling constant. We have chosen to change the Coulomb potential in order to explore its influence on the required values of the EIP coupling constant because these are in fact the most uncertain parameters. As expected, we see that, whereas the ordinary strong coupling theory requires EIP coupling constants greater than those of Yamaji's model, the non adiabatic theory of PS requires lower values.

However, all the calculations agree in showing that the values of the EIP coupling constant must be non negligible nor small: this in turn implies that the EMV coupling alone does not suffice to yield critical temperatures in the correct range for the BEDT–TTF based organic conductors. On the other hand, the converse is also true. Without a contribution from the EMV coupling one would require EIP constants that appear to be too large compared with the presently available estimates. In this respect, these estimates are best approached by our calculations when the non adiabatic PS model is used.

ISOTOPIC EFFECT CALCULATIONS

In this section we report an analysis of the effects produced by the isotopic substitution of the carbon atoms in the central and external double bonds of a TTF based molecule. Such an analysis has been stimulated by the experimental results recently reported for the effect on T_c of the isotopic substitution of ^{12}C with ^{13}C in the central double bond of the BEDT–TTF molecules in β and κ phase superconducting salts.[3,4] These appear to be key experiments for assessing the importance of the EMV coupling for organic superconductivity. In fact, this type of isotopic substitution should have the greatest effect on T_c if the pairing is dominated by the EMV coupling. Unfortunately different results have been obtained by the two reported experiments[3,4] and have led to conflicting conclusions as to the relative importance of the EMV and EIP couplings.

To improve our knowledge of the isotopic effect in organic superconductors and to give a firm basis to the theoretical discussion of the experimental results it is important to carry out a correct analysis of the molecular vibrations affected by the substitution. The two vibrational a_g modes of the BEDT–TTF molecule that are most influenced by substitution of the two carbon atoms in the central double bond are the ν_3 and ν_4 modes.[15] They can be approximately described in terms of a fifty–fifty mixing of the stretching vibrations of the internal and external double bonds of the TTF skeleton with opposite relative phases. For the neutral molecule the observed frequencies of the two modes are 1554 and 1494 cm^{-1}, respectively, and their isotopic shifts exhaust the isotopic product rule[23,4] for ^{13}C substitution.

Based on the above considerations, our analysis of the isotopic effect considers only the stretching vibrations of the double bonds, thus reducing the problem to that of two coupled oscillators. This simple model allows us to calculate, for the ν_3 and ν_4 modes, the frequencies and the EMV coupling constants renormalized by the isotopic substitution. We define the two totally symmetric coordinates

$$S_1 = R_1 \quad , \quad S_2 = \frac{1}{\sqrt{2}}(R_2 + R_3) \tag{16}$$

where R_1, R_2 and R_3 are the internal stretching coordinates of the central and the two external double bonds, respectively. The corresponding GF matrix is

$$\mathbf{GF} = \begin{pmatrix} 2K(M_1)^{-1} & 2K_{1,2}(M_1)^{-1} \\ 2K_{1,2}(M_2)^{-1} & 2K(M_2)^{-1} \end{pmatrix}, \tag{17}$$

where M_1 and M_2 are the masses of the carbon atoms forming the central and external double bonds, respectively. In defining the GF matrix we have assumed a simplified force field where the two oscillators, S_1 and S_2, have the same force constant, $K = K_{1,1} = K_{2,2}$, and $K_{1,2}$ is the coupling force constant between the two oscillators.

For the case where $M_1 = M_2 = M$, the solution of the simple vibrational problem gives the normal mode frequencies and the corresponding dimensionless normal coordinates

$$\omega_i = \sqrt{\frac{2}{M}}(K \pm K_{1,2})^{1/2} \qquad i = 1,2, \tag{18.a}$$

$$Q_i = \sqrt{\frac{\omega_i M}{2\hbar}}(S_1 \pm S_2)^{1/2} \qquad i = 1,2. \tag{18.b}$$

Knowing the frequencies ω_i of the unsubstituted molecule, through the relations (18.a) it is possible to find the values of the force constants K and $K_{1,2}$ that remain the same for the substituted one. On the basis of this force field it is possible to calculate the frequencies ω'_i and the normal coordinates Q'_i for the case $M_1 \neq M_2$. The renormalized frequencies, for $i = 1,2$, are

$$(\omega'_i)^2 = K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \left[K^2\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4}{M_1M_2}(K^2 - K^2_{1,2})\right]^{1/2}. \tag{19}$$

The solution of the vibrational problem for $M_1 \neq M_2$ gives the transformation matrix $\mathbf{L}'$ that relates the new dimensionless normal coordinates Q'_i to the symmetry coordinates S_i as $\mathbf{S} = \mathbf{L}'\,\mathbf{Q}'$. From this relation and the matrix form of Eq.s (18.b), $\mathbf{Q} = \mathbf{L}^{-1}\mathbf{S}$, we are able to define the transformation matrix $\mathbf{D}$ that relates the normal coordinates Q'_i of the isotopically substituted molecule to the coordinates Q_i of the unsubstituted one according to

$$\mathbf{Q} = \mathbf{L}^{-1}\mathbf{L}'\mathbf{Q}' = \mathbf{D}\mathbf{Q}'. \tag{20}$$

From Eq. (20) the relations between the new dimensionless EMV coupling constants λ'_i, renormalized by isotopic substitution, and those of the unsubstituted molecule follow straightforwardly. In fact by their definition, see Eq. (1), we can express the new dimensional EMV coupling constants as

$$g'_i = \left(\frac{\partial\epsilon}{\partial Q'_i}\right)_\circ = \left(\frac{\partial\epsilon}{\partial Q_1}\right)_\circ \frac{\partial Q_1}{\partial Q'_i} + \left(\frac{\partial\epsilon}{\partial Q_2}\right)_\circ \frac{\partial Q_2}{\partial Q'_i}, \qquad (i = 1,2), \tag{21}$$

and, using the Eq. (20) as

$$g'_i = g_1 D_{1,i} + g_2 D_{2,i} \qquad i = 1,2. \tag{22}$$

The corresponding dimensionless EMV coupling constants, Eq. (8), are

$$\lambda'_i = \left(\frac{\omega_1}{\omega'_i}\right) D^2_{1,i}\lambda_1 + \left(\frac{\omega_2}{\omega'_i}\right) D^2_{2,i}\lambda_2 + 2\frac{(\omega_1\omega_2)^{1/2}}{\omega'_i} D_{1,i}D_{2,i}(\lambda_1\lambda_2)^{1/2}, \tag{23}$$

for $i = 1,2$, the unitarity of the involved transformations implies that $\lambda'_1 + \lambda'_2 = \lambda_1 + \lambda_2$.

Table II collects the frequencies ω_i and the EMV coupling constants λ_i for the ν_3 and ν_4 modes of the TMTTF molecule bearing an average charge +0.5.[11,7] ω'_i and λ'_i are the corresponding values calculated for the molecule substituted with ^{13}C in the central double bond, while ω''_i and λ''_i are those of the fully substituted molecule. As expected, the isotopic shift is greater for the fully substituted molecule whereas $\lambda''_i = \lambda_i$ since the normal coordinates do not change.

TABLE II Estimated isotopic effects on the frequencies and the EMV coupling constant for the ν_3 and ν_4 a_g modes of TMTTF.

a_g mode	ω_i (cm^{-1})	λ_i	ω'_i (cm^{-1})	λ'_i	ω''_i (cm^{-1})	λ''_i
ν_3	1603	0.0102	1579	0.0375	1540	0.0102
ν_4	1478	0.1769	1442	0.1496	1420	0.1769

TABLE III Calculated isotopic T_c shifts.

Model	$\Delta T'_c/T_c$ (%)	$\Delta T''_c/T_c$ (%)
Yamaji	−0.1, −0.1	0.8, 0.2
McMillan	−0.4, −0.3	−1.2, −1.1
PS	−0.7, −0.6	−2.7, −2.0

Table III reports the T_c shifts, $\Delta T'_c/T_c$ and $\Delta T''_c/T_c$, calculated with the the Yamaji, McMillan and PS models for the molecule substituted in the central and in all the double bonds respectively. As for the previous calculations, the experimental data of the TMTTF molecule have been employed, the band parameters have been defined through an effective charge transfer integral of 0.20 eV, and the frequency of the coupled intermolecular mode has been fixed to 50 cm^{-1}. For the dimensionless EIP coupling constant we have chosen the values required to give a T_c of 10 K for the unsubstituted molecule with an on–site Coulomb potential ranging from 0.30 to 0.60 eV. The reported T_c shifts refer to $U = 0.30$ eV (left values) and to $U = 0.60$ eV (right values). While the Yamaji model gives opposite shifts for the two substitutions, the other two models give negative T_c shifts that are greater for the fully substituted molecule. For the substitution in the central double bond only the calculated shifts are negative and less than 1% in all cases. Only the McMillan and PS models give negative T_c shifts greater than 1% for the fully substituted molecule.

The main qualitative conclusion of the present model calculation is that very small negative isotopic T_c shifts are predicted even when the contribution of the EMV couplings is taken into account on realistic grounds. Thus, whereas the negative results reported for the κ phases[4] do not rule out a role of the molecular vibrations, the anomalously large isotopic shift reported[3] for β_H-(BEDT-TTF)$_2$I$_3$ is difficult to reconcile with the models considered here for phonon driven superconductivity. Further measurements on the fully substituted materials could provide a critical test of the PS model since the predicted T$_c$ shift is well above the experimental uncertainties.[4]

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