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Electron phonon interactions and superconductivity in α'-TTF[Pd(dmit)$_2$]$_2$

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Abstract. A simple model is developed to understand superconductivity in α'-TTF[Pd(dmit)$_2$]$_2$. We include electron-*intra* molecular and *inter*molecular phonon interactions as the mechanism of superconductivity. *Intra*molecular vibrations included are the eight symmetric A_g modes of the Pd(dmit)$_2$ molecule. *Inter*molecular vibrations included are the longitudinal acoustic and transverse acoustic (LA and TA) modes of the Pd(dmit)$_2$ column. All the electron-phonon coupling constants are calculated from first principles. We find that largest el-*intra*molecular vibration coupling is to the A_g mode with the highest frequency (1449 cm^{-1}). The el-*inter*molecular coupling to the LA mode is found to be larger than the *total* el-*intra*molecular couplings. We also find el-(TA)phonon coupling to be at least an order of magnitude smaller than el-(LA)phonon coupling. Estimate of superconducting transition temperature is comparable to experimental result. We also provide a detailed discussion, employing the results of recent numerical calculations on two-chain Hubbard model and the specific material parameters, on the relative importance of el-ph and Coulomb-origin mechanisms of superconductivity in α'-TTF[Pd(dmit)$_2$]$_2$ and TTF[Ni(dmit)$_2$]$_2$.

PACS. 74.70.Kn Organic superconductors – 74.20.-z Theories and models of superconducting state – 63.20.Kr Phonon-electron and phonon-phonon interactions – 74.20.Fg BCS theory and its development

1 Introduction

Ever since the theoretical suggestion by Little [1], in 1964, regarding the possibility of an exciton mechanism of high temperature superconductivity in a hypothetical conducting polymer chain (with polarizable molecules attached to the spine), search for high temperature organic superconductors has been a vigorous field of research [2–4]. Though Little's superconductor has not been synthesized so far, the possibility of high superconducting transition temperatures inspired investigations into the synthesis [5] of organic conductors which eventually led to the synthesis of quasi-one-dimensional (Q1D) TMTSF molecule based charge-transfer compounds (now well known as Bechgaard salts) by Bechgaard *et al.,* and consequently to the discovery [6] of the first organic superconductor (TMTSF)$_2$PF$_6$ (with a T_c of 1.2 K under a pressure of 6.5 Kbar) by Jérome *et al.,* in 1980. A large number of organic superconductors with varying degrees of dimensionality has been discovered since then.

In this paper, we focus on investigating the interactions responsible for superconductivity in Q1D organic superconductor α'-TTF[Pd(dmit)$_2$]$_2$ discovered [7] by Brossard *et al.* In most of the currently known organic superconductors [2], the conduction band is formed by the overlapping of HOMOs (Highest Occupied Molecular Orbital) or LUMOs (Lowest Unoccupied Molecular Orbital) of nearest-neighbor (NN) radical cations or anions, respectively, in the solid. However, an important feature of the electronic structure of TTF[M(dmit)$_2$]$_2$ (where M = Ni or Pd) solids is that band structure calculations [8] and experimental investigations [9] have clearly shown that both HOMO and LUMO derived bands cross the Fermi level. In a recent paper [10], we presented a theory of superconductivity in TTF[Ni(dmit)$_2$]$_2$ based on such bands and including the electron *intra*, *inter*molecular vibration interactions and a pair-transfer process originating from the Coulomb interaction between two electrons on a Ni(dmit)$_2$ molecule. Brossard *et al.* were the first to discover [7] that α'-TTF[Pd(dmit)$_2$]$_2$ becomes superconducting at a T_c of 6.5 K under 20 Kbar. In the α'-TTF[Pd(dmit)$_2$]$_2$ solid, TTF and Pd(dmit)$_2$ molecules are stacked in columns parallel to the b-axis [7,11]. These columns form alternate sheets of TTF and Pd(dmit)$_2$ parallel to the b-c plane. In α'-TTF[Pd(dmit)$_2$]$_2$ an electron transfer occurs from TTF to Pd(dmit)$_2$ so that the charge carriers are on the Pd(dmit)$_2$ columns. Electrical resistivity

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measurements [7] indicate that superconducting instability is occurring in a Fermi liquid normal state.

This paper is organized as follows. Our model for Pd(dmit)$_2$ column and the mean field theory of superconductivity is presented in Section 2, a discussion of the relative importance of Coulomb origin mechanism of superconductivity and electron-phonon mechanism is given in Section 3 and the conclusions are given in Section 4.

2 Mean-field theory of superconductivity in α'-TTF[Pd(dmit)$_2$]$_2$

In our model to understand superconductivity in α'-TTF[Pd(dmit)$_2$]$_2$, we confine ourselves to the Pd(dmit)$_2$ column. Observation [12,13] of superconductivity in N(CH$_3$)$_4$[Ni(dmit)$_2$]$_2$ at 5 K (under 7 Kbar) clearly indicates that *TTF* columns are not essential for superconductivity to develop in the M(dmit)$_2$ columns. In our model for α'-TTF[Pd(dmit)$_2$]$_2$, we include both electron *intra* and *inter*molecular phonon interactions as the primary origin of superconductivity. The unique feature in the band structure of this material leads to a pair-transfer between the HOMO and LUMO derived bands and is included in our model. We use a two-chain Hubbard type model for a single column of Pd(dmit)$_2$. Each dmit unit (of the two units in a Pd(dmit)$_2$ molecule) is taken as a site in the model, so that a stack of Pd(dmit)$_2$ gives rise to a pair of bonding and antibonding bands corresponding to HOMO and LUMO bands. Including *intra*molecular vibrations (the eight A_g modes with frequencies ω_μ) of the Pd(dmit)$_2$ molecule and the *inter*molecular vibrations (the longitudinal and transverse acoustic modes of the Pd(dmit)$_2$ column with frequencies $\omega_{q\nu}$), our model for a Pd(dmit)$_2$ column is:

$$\begin{aligned} H = &\sum_{ji\sigma} \epsilon_i C^\dagger_{ji\sigma} C_{ji\sigma} - \sum_{i\sigma} t_{di}\left(C^\dagger_{1i\sigma} C_{2i\sigma} + \text{h.c.}\right) \\ &- \sum_{ji\sigma} t_{i,i+1}\left(C^\dagger_{ji\sigma} C_{j,i+1,\sigma} + \text{h.c.}\right) + U\sum_{ji} n_{ji\uparrow} n_{ji\downarrow} \\ &+ \sum_{i\mu} \omega_\mu (b^\dagger_{i\mu} b_{i\mu} + \frac{1}{2}) + \sum_{q\nu} \omega_{q\nu}\left(b^\dagger_{q\nu} b_{q\nu} + \frac{1}{2}\right)\cdot \end{aligned} \quad (1)$$

Here $j(=1,2)$ is the chain index and i is the site index. ϵ_i, t_{di} and $t_{i,i+1}$ are the site energy of dmit, the electron transfer energy between dmit units on the same rung, and that between dmit's on NN sites along the same chain, respectively. This modeling is based on the fact that the HOMO and LUMO can be regarded as the bonding and antibonding combinations of the same type of molecular orbitals at two dmit units in a Pd(dmit)$_2$ molecule. We first convert H in terms of $c_{1i\sigma} = \frac{1}{\sqrt{2}}(\alpha_{1i\sigma} + \alpha_{2i\sigma})$ and $c_{2i\sigma} = \frac{1}{\sqrt{2}}(\alpha_{1i\sigma} - \alpha_{2i\sigma})$ to obtain $H = H_0 + H_1$, where

$$H_0 = \sum_{li\sigma} E_{li} \alpha^\dagger_{li\sigma}\alpha_{li\sigma} - \sum_{li\sigma} t^{(l)}_{i,i+1}(\alpha^\dagger_{li\sigma}\alpha_{l,i+1,\sigma} + \text{h.c.}), \quad (2)$$

and

$$\begin{aligned} H_1 = U_m &\sum_{li}(n_{li\uparrow}n_{li\downarrow} + n_{li\uparrow}n_{\tilde{l}i\downarrow} + \alpha^\dagger_{li\uparrow}\alpha^\dagger_{\tilde{l}i\downarrow}\alpha_{li\downarrow}\alpha_{\tilde{l}i\uparrow} \\ &+ \alpha^\dagger_{li\uparrow}\alpha^\dagger_{li\downarrow}\alpha_{\tilde{l}i\downarrow}\alpha_{\tilde{l}i\uparrow}) + \sum_{i\mu}\omega_\mu\left(b^\dagger_{i\mu}b_{i\mu} + \frac{1}{2}\right) \\ &+ \sum_{q\nu}\omega_{q\nu}\left(b^\dagger_{q\nu}b_{q\nu} + \frac{1}{2}\right)\cdot \end{aligned} \quad (3)$$

Here $\tilde{l} = (3-l)$, $U_m = \frac{U}{2}$, with U being the on-site Coulomb energy at a dmit group, $n_{li\sigma} = \alpha^\dagger_{li\sigma}\alpha_{li\sigma}$ and $E_{li} = \left(\epsilon_i - (-1)^{l+1}t_{di}\right)$. In equations (2, 3), l refers to HOMO($l = 1$) and LUMO($l = 2$) *levels* of a Pd(dmit)$_2$ molecule and $t^{(l)}_{i,i+1}$ are the HOMO-HOMO and LUMO-LUMO transfer energies between two NN orbitals.

We expand HOMO and LUMO levels in terms of normal mode coordinates (Q_μ) of Pd(dmit)$_2$ molecule and $t^{(l)}_{i,i+1}$ in terms of lattice displacements (u_ν) corresponding to *inter*molecular vibrations to obtain el-ph couplings. Since according to band structure calculations [8] the position of the Fermi level is such that the LUMO band is *close* to half-filled and the HOMO band is *close* to fully filled situation, the LUMO band electrons are strongly coupled to the *inter*molecular phonons and the HOMO electrons have only negligible coupling to *inter*molecular phonons. After eliminating the phonons to generate phonon mediated el-el interactions, treating U_m dependent terms in a mean-field approximation, and retaining pair-transfer term originating from the fourth term in equation (3), and employing BCS mean-field approximations [14], the superconducting transition temperature is obtained (for details see Ref. [10]) to be $T_\text{c} = 1.13\,\omega_\text{D}\,\text{e}^{-\frac{1}{\lambda_\text{eff}}}$, where

$$2\lambda_\text{eff} = (\lambda_1 + \lambda_2) + \sqrt{(\lambda_1 - \lambda_2)^2 + 4\mu^*_1\mu^*_2}\ ; \quad (4)$$

$$\begin{aligned} \lambda_1 &= N_\text{HOMO}\sum_\mu \frac{1}{\omega_\mu}\left|\frac{\partial E_\text{HOMO}}{\partial Q_\mu}\right|^2 - \mu^*_1 \\ &= \sum_\mu \lambda^\text{intra}_\text{HOMO}(\mu) - \mu^*_1 \end{aligned} \quad (5)$$

and

$$\begin{aligned} \lambda_2 = &\sum_\mu \frac{N_\text{LUMO}}{\omega_\mu}\left|\frac{\partial E_\text{LUMO}}{\partial Q_\mu}\right|^2 \\ &+ \sum_\nu \frac{16\ N_\text{LUMO}}{m\omega^2_\nu}\left|\frac{\partial t_\text{LUMO}}{\partial u_\nu}\right|^2 - \mu^*_2 \\ = &\sum_\mu \lambda^\text{intra}_\text{LUMO}(\mu) + \sum_\nu \lambda^\text{inter}_\text{LUMO}(\nu) - \mu^*_2. \end{aligned} \quad (6)$$

$$\mu^*_l = \frac{N_l U_m}{1 + U_m\sum_{l'} I_{l'} N_{l'}}\ ; \quad (7)$$

$$I_l = \ln\left(\frac{\sqrt{D^2_l - t^2_d}}{\omega_\text{D}}\right)\cdot \quad (8)$$

In the above equations D_l, N_l and ω_D are the

Table 1. Theoretically calculated electron-*intra*molecular vibration (BCS) coupling constants for HOMO and LUMO electrons in Pd(dmit)$_2$.

$\omega_\mu(\mathrm{cm}^{-1})$	$\lambda^{\mathrm{intra}}_{\mathrm{HOMO}}(\mu)$	$\lambda^{\mathrm{intra}}_{\mathrm{LUMO}}(\mu)$
1449	0.085	0.073
1227	0.011	0.007
1068	0.002	0.008
588	0.014	0.006
563	0.023	0.016
456	0.004	0.002
388	0.025	0.028
132	0	0

half-band widths, one-electron-single-spin DOS's (at the Fermi level), ω_{D} is the Debye temperature and 1 and 2 refers to HOMO and LUMO, respectively. Now, we have to estimate the el-ph (BCS)coupling constants.

The el-ph coupling constants to be calculated are sixteen (eight each for HOMO and LUMO electrons) el-(A_g) *intra*molecular phonon coupling constants and el-*inter*molecular phonon (longitudinal and transverse vibrations of the Pd(dmit)$_2$ molecule in the molecular chain) coupling constants. The el-*intra*molecular vibration coupling constants ($\lambda^{\mathrm{intra}}_{\mathrm{HOMO}}(\mu)$ and $\lambda^{\mathrm{intra}}_{\mathrm{LUMO}}(\mu)$ for eight A_g modes of the Pd(dmit)$_2$ molecule) are calculated in the following way [15]. First we calculate the electronic structure of Pd(dmit)$_2$ in its equilibrium configuration. Next we calculate the molecular vibrational frequencies and atomic displacements. Finally, we distort the molecule (according to the atomic displacements corresponding to each A_g mode) and again calculate the electronic structure of the distorted structure. From the changes in the HOMO and LUMO level positions (and using Eqs. (5) and (6) and one-electron DOS's [8,16] $N_1 = 1.178/(\mathrm{eV, spin})$ and $N_2 = 0.914/(\mathrm{eV, spin})$) el-*intra*molecular vibration coupling constants are calculated. This procedure is repeated for all the eight A_g modes for HOMO and LUMO electrons. The electronic structure of Pd(dmit)$_2$ is calculated using extended Hückel method. The parameters used in these calculations are the same as those used by Canadell *et al.* [8] Atomic positions taken from reference [17] were used to construct (by taking averages of similar bond-angles and bond-lengths) a symmetric structure and this was used for the calculations of electronic structure. The normal modes calculation was performed using Gaussian-98 [18]. Out of the 45 optical modes of Pd(dmit)$_2$, 8 are totally symmetric A_g modes.

The frequencies of the A_g modes and the coupling constants are shown in Table 1. The strongest el-*intra*molecular molecular vibration (BCS) coupling is found to be to the A_g mode with the highest frequency. A similar result was obtained [10] for the isostructural Ni(dmit)$_2$ and this result is consistent with the experimental estimates made by Liu *et al.* [19], and has also received confirmation from the recent Raman scattering studies [20] by Pokhodnya *et al.*

Next we turn to the calculation of el-*inter*molecular vibration coupling constants. The three possible vibrational modes of a uniform column of Pd(dmit)$_2$ are one longitudinal acoustic (LA) mode and two transverse acoustic (TA) modes (along the long and short axes of the molecule). The el-(LA)phonon coupling constant is obtained by changing the relative separation between NN molecules and then calculating the change (due to the changes in the molecular wave function overlap when the molecules perform LA vibration) in electron transfer energy between NN molecules. To obtain el-(TA)phonon coupling constant, we change the relative transverse (to the Pd(dmit)$_2$ column axis) position of the NN molecules and calculate the changes in the electron transfer energy between NN molecules. For LUMO band electrons, we obtained $\lambda^{\mathrm{inter}}_{\mathrm{LUMO}} \approx 0.5$ for LA-phonon. We find that $\lambda^{\mathrm{inter}}_{\mathrm{LUMO}} \approx 0.02$ for TA-phonons. As mentioned before, the HOMO band is *close* to fully filled and due to the band-filling dependence of the el-(*inter*molecular)ph interaction, the HOMO band el-*inter*molecular vibration coupling is negligible.

All the sixteen el-*intra*molecular (BCS) coupling constants and the two intermolecular vibration (BCS) coupling constants are now available from our computations. The values of $2D_1$, $2D_2$, DOS's, t_d, and U_m are 0.8 eV, 0.8 eV, $N_1 = 1.178/(\mathrm{eV, spin})$, $N_2 = 0.914/(\mathrm{eV, spin})$, 0.1875 eV and 1 eV, respectively. Using these values, calculated values of λ_1 and λ_2, the superconducting transition temperature (T_{c}) is calculated to be 12 K (where we used $\omega_{\mathrm{D}} = 60$ K, a value within the range normally found in organic superconductors [21,22]). The experimental value of T_{c} of α'-TTF[Pd(dmit)$_2$]$_2$ is 6.5 K (under 20 Kbar). While comparing theoretical estimate with the experimental values, it should be borne in mind that calculations are done considering the room temperature equilibrium structural parameters. While el-*intra*molecular interaction energies are unlikely to be seriously affected by application of pressure, *inter*molecular overlaps and consequently el-*inter*molecular interaction energies would be affected. There will also be pressure induced changes in the DOS's. It should be noted that a unique single superconducting transition temperature for a two-band superconductor (with significantly different coupling constants for electrons in the two bands) obtains due to the presence of pair-transfer terms in the original Hamiltonian. The pair-transfer term has an important effect of reducing the destructive effect (on T_{c}) of *intra*-band Coulomb repulsion. In fact, when $\lambda_1 = \lambda_2 = \lambda$ and $N_1 = N_2$, the pair-transfer term completely cancel the *intra*-band Coulomb pseudopotentials as can be easily seen from equation (4) since in this case $\lambda_{\mathrm{eff}} = \lambda$. So, even though the U_m is not small (say, compared to the band-width), pair-transfer process, originating from this term in the Hamiltonian of our two-band superconductor, has the effect of reducing the effect of *intra*-band Coulomb repulsion. In the absence of these terms, the two bands decouple and since the band characteristics and coupling constants are different, the model will lead to two separate T_{c}'s. At present, there is no experimental evidence for two separate superconducting transitions in α'-TTF[Pd(dmit)$_2$]$_2$.

It is useful to compare the el-ph couplings obtained for α'-TTF[Pd(dmit)$_2$]$_2$ and TTF[Ni(dmit)$_2$]$_2$ to see if it is possible to understand the difference in superconducting transition temperatures (6.5 K for the former and 1.6 K for the later) in these materials. For α'-TTF[Pd(dmit)$_2$]$_2$ we have: $V_1^{\rm ph}(\text{intra}) = N_{\rm HOMO}^{-1}\sum_\mu \lambda^{\rm intra}_{\rm HOMO}(\mu) = 140$ meV, $V_2^{\rm ph}(\text{intra}) = N_{\rm LUMO}^{-1}\sum_\mu \lambda^{\rm intra}_{\rm LUMO}(\mu) = 154$ meV and $V_2^{\rm ph}(\text{inter}) = N_{\rm LUMO}^{-1}\lambda^{\rm inter}_{\rm LUMO} = 550$ meV and for TTF[Ni(dmit)$_2$]$_2$ we have [10]: $V_1^{\rm ph}(\text{intra}) = 145$ meV, $V_2^{\rm ph}(\text{intra}) = 137$ meV, and $V_2^{\rm ph}(\text{inter}) = 320$ meV. From this comparison, we can infer that at least one of the factors leading to larger $T_{\rm c}$ in α'-TTF[Pd(dmit)$_2$]$_2$ is the larger value of el-*inter*molecular LA-phonon coupling. One possible reason for this is the smaller value of separation (between NN molecules) along b-axis (the M(dmit)$_2$ column axis) in the α'-TTF[Pd(dmit)$_2$]$_2$ (3.608 Å) compared to that (3.732 Å) in TTF[Ni(dmit)$_2$]$_2$. Note also that el-(LA)ph coupling is larger in α'-TTF[Pd(dmit)$_2$]$_2$ compared to TTF[Ni(dmit)$_2$]$_2$ even though the DOS's ($N_{\rm HOMO}$ and $N_{\rm LUMO}$) at the Fermi level are smaller in the former (1.178/(eV, spin) and 0.91/(eV, spin)) compared to in the later (1.53/(eV, spin) and 1.25/(eV, spin)).

3 Electron-phonon vs. Coulomb origin mechanism of superconductivity in TTF[M(dmit)$_2$]$_2$ (where M = Ni or Pd) compounds

In the past, based on the finding of superconducting correlations in exact diagonalization studies [23] of two-chain (2C) Hubbard model (with repulsive interactions), one of the present authors and his collaborators have proposed that superconductivity in TTF[M(dmit)$_2$]$_2$ (where M is Ni or Pd) compounds may be originating from Coulomb interaction. These calculations were done on small systems (2×6 sites). Later, more extensive calculations [24,25] on larger systems (2×72 sites) were performed using variational Monte Carlo method. These calculations did confirm the existence of finite bulk limit of superconducting condensation energy in 2C-Hubbard model. Properties of the 2C-Hubbard model depends on the values of n (the number of electrons per site), $\frac{t_d}{t}$ (where t_d is the inter-chain hopping energy between nearest neighbor sites and t is the intra-chain hopping between nearest neighbor sites) and $\frac{U}{t}$ (where U is the Coulomb repulsion between opposite spin electrons on a site). For the 2C-Hubbard model, Koike *et al.* found that, for $\frac{U}{t} = 8$ and $n = \frac{5}{6} \approx 0.833$, for superconductivity to exist in the 2C-Hubbard model the relative band position should be such that the bottom of the upper band is very close to the Fermi level which lies in the lower band, in which case $\frac{t_d}{t}$ is in a narrow range around 1.4. Noack *et al.* [26] have performed studies of 2C-Hubbard model employing the Density Matrix Renormalization Group (DMRG) method. For $\frac{U}{t} = 8$ and n = 0.75, 0.875 and 0.9375, superconducting correlations was found to be largely enhanced in a narrow range of t_d around 1.33, 1.4, and 1.45, respectively, with this maximum increasing with increasing n.

Applicability of these results to TTF[M(dmit)$_2$]$_2$ superconductors deserves a careful consideration of the band filling and relative positions of HOMO and LUMO bands in these materials. By comparing band structure calculations [8] with CDW transitions at ambient pressure, it was inferred that the average number of electrons per dmit site is approximately 1.19 in α'-TTF[Pd(dmit)$_2$]$_2$ and 1.25 in TTF[Ni(dmit)$_2$]$_2$ and the Fermi level lies in the midst of the LUMO band and slightly cuts the top of the HOMO band. If we make the electron-hole reversal this band position is close to the above mentioned one which is ideal for pair-transfer mechanism to drive superconductivity. The n values, 0.81 and 0.75, are also close. We should also have an estimate of $\frac{U}{t}$ in these materials. From optical conductivity measurements [20] on [NBu$_4$][Ni(dmit)$_2$], U_m was estimated to be 0.948 eV. In another estimate [27] of U_m, DMRG calculations on a model for NH$_2$Me$_2$[Ni(dmit$_2$]$_2$ were compared to experimental activation energy of semiconducting NH$_2$Me$_2$[Ni(dmit)$_2$]$_2$ [28] to obtain 1.16 eV for U_m. Thus the value of $\frac{U}{t}$ is in the range 9–10, which is close to the value used in numerical calculations. Estimation of t_d and t is delicate. One way to do so is to fit bands of the simple two-chain model to the results of band structure calculations, Figures 3 and 4, in reference [8]. This fitting provides $t_d \approx 0.1875$ eV and $t \approx 0.2$ eV for α'-TTF[Pd(dmit)$_2$]$_2$ and $t_d \approx 0.2$ eV and $t \approx 0.1625$ eV for TTF[Ni(dmit)$_2$]$_2$. Thus, the values of $\frac{t_d}{t}$ seems to lie in the range of 0.9–1.3. Now, as mentioned in the previous paragraph, Noack *et al.*'s DMRG calculations show that as the value of $\frac{t_d}{t}$ decreases from 1.4 the peak in pairing response shifts to lower values of n, but at the same time the maximum pairing correlation reduces rapidly. So, considering together the calculations presented in this paper, that given in reference [10], recent numerical studies of 2C-Hubbard model and that we are able to get a qualitative understanding of the reason for the increase of $T_{\rm c}$ in α'-TTF[Pd(dmit)$_2$]$_2$ compared to that in TTF[Ni(dmit)$_2$]$_2$, we judge that in TTF[M(dmit)$_2$]$_2$ (where M is Ni or Pd) superconductors, the el-ph interactions provide the glue for electron pairing and that the Coulomb-origin pair-transfer process is not so powerful as to drive superconductivity by itself and plays the helping role to the el-ph mechanism by substantially reducing the destructive effect of *intra*-band Coulomb repulsion.

Involvement or otherwise of pair-transfer process can be tested by tunneling measurements since in the presence of it, the bands are coupled and superconducting gaps will open up in both HOMO and LUMO bands at a single superconducting $T_{\rm c}$. On the other hand, should they be not involved, then the bands decouple and since *inter*-molecular phonons have only a negligible coupling to the HOMO band electrons the $T_{\rm c}^{\rm HOMO}$ is practically zero and consequently only the LUMO band will develop a superconducting energy gap (actually a pseudo-gap in the total density of states since both HOMO and LUMO bands overlap) at $T_{\rm c}$.

4 Conclusions

In this paper we presented a BCS−type mean-field theory of superconductivity in α'-TTF[Pd(dmit)$_2$]$_2$. In our model we included el-*intra* and *inter*molecular vibrations couplings as the mechanism of superconductivity in this material. The unique band structure of this material (with both HOMO and LUMO derived bands crossing the Fermi level) leads to a pair-transfer process and this leads a unique superconducting transition temperature for this two-band superconductor. We performed a complete normal mode analysis of the Pd(dmit)$_2$ molecule and all the el-*intra* and *inter* molecular phonon coupling constants were calculated from first principles. It is found that el-*inter*molecular coupling for LA phonon is larger than the *total* el-*intra* molecular phonon couplings. The coupling between electrons and TA-phonons is found to be at least an order of magnitude smaller than that for LA phonons. Among el-*intra*molecular A_g-mode couplings, it is found that the strongest coupling is to the A_g-mode with the highest frequency ($1449\,\mathrm{cm}^{-1}$). The $1449\,\mathrm{cm}^{-1}$ mode is the one in which inner four Carbon atoms move, in the molecular plane, transverse to the long-axis of the Pd(dmit)$_2$ molecule (see Ref. [10]). The estimate of superconducting transition temperature based on these coupling constants is comparable to the experimental results. Further, by comparing the el-ph coupling constants obtained in this paper for α'-TTF[Pd(dmit)$_2$]$_2$ and those in reference [10] for TTF[Ni(dmit)$_2$]$_2$, we found that at least one source of larger T_c of the former is the larger value of el-*inter* molecular LA-phonon coupling. We also examined the material parameter values to see if the Coulomb-origin mechanism plays an important role in driving superconductivity in TTF[M(dmit)$_2$]$_2$ or not. The answer is almost certainly negative. On the basis of this consideration, the studies presented in this paper and that in reference [10], we clarified that the origin of superconductivity in TTF[M(dmit)$_2$]$_2$ (where M is Ni or Pd) is from a cooperative effect of el-ph interactions and the pair transfer process (which almost cancels the Coulomb pseudo potential in each band) as the most consistent scenario at present.

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