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Interstack spin-orbit coupling and ESR line broadening in tetrathiafulvalenium tetracyanoquinodimethanide (TTF-TCNQ)

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Spin-orbit-coupled electronic transitions between donor and acceptor conduction bands are shown to account for the ESR linewidth in tetrathiafulvalenium tetracyanoquinodimethanide (TTF-TCNQ) and similar compounds. Slight admixture of in-plane (σ) donor orbital character into the acceptor conduction (π) bands via the overlap of these orbitals is essential, since the donor heavy atom spin-orbit interaction mixes effectively only donor σ and π orbitals. The corresponding spin-orbit transitions within or between donor stacks are usually symmetry forbidden, which result is significant for the one-stack salts.

Despite extensive electron-spin resonance (ESR) investigations of one-dimensionally conducting organic charge-transfer compounds such as tetrathiafulvalenium tetracyanoquinodimethanide (TTF-TCNQ) and its isostructural selenium analog TSeF-TCNQ, their ESR line broadening (ΔH) mechanism is not well understood.[1] Experiment shows ΔH is due to donor chalcogen (S or Se) spin-orbit interactions,[1] denoted $H_{\text{ch}}^{(\text{so})}$, but symmetry restrictions limit spin-orbit scattering in a one-dimensional band.[2] Thus, the ΔH mechanism requires weak interstack interactions, as recognized by theories based on dimensionally restricted modifications of spin-orbit relaxation in isotropic metals.[2] This approach, however, partially neglects a key fact: namely, that the one-center matrix elements of $H_{\text{ch}}^{(\text{so})}$ between S or Se valence atomic orbitals (AO's), compared to which all other spin-orbit terms are negligible, couple the π molecular orbitals (MO's) of the donor conduction-band states only to in-plane S or Se σ AO's.[3] Thus, difficulties associated with mixing these energetically and spatially dissimilar π and σ orbitals further restrict the already symmetry-restriced spin-orbit scattering within an isolated donor stack. Moreover, and contrary to the dimensionally restricted isotropic metal models, the required interstack interaction cannot be supplied by π_{donor}-π_{acceptor}-type integrals such as the interstack transfer integral $t_{\perp}$.[2] Here we show that the acceptor π states acquire small amounts of donor σ character via overlap between the donor σ and acceptor π AO's, enabling spin-orbit-coupled transitions between adjoining donor and acceptor conduction-band states. Also, the unexpectedly small angular dependence of ΔH on external magnetic field ($\vec{H}$) in TTF-TCNQ,[1] despite its highly anisotropic crystal structure,[4] will suggest its transitions are predominantly (filled donor state) ⟷ (donor, acceptor pair).

Figure 1 depicts for TTF-TCNQ the effect of the chalcogen spin-orbit interactions and the consequences of overlap between the acceptor π AO's and the S or Se $p\sigma$ donor AO's. For a given S or Se atom $H_{\text{ch}}^{(\text{so})} = \lambda \vec{l} \cdot \vec{s}$ where $\lambda/\hbar = 7.2 \times 10^{13}$ and 3.8×10^{14} sec^{-1} for S $3p$ and Se $4p$ AO's, respectively,[5] and $\hbar\vec{s}$ and $\hbar\vec{l}$ are the electron-spin and orbital angular momenta. For the molecular coordinates depicted in Fig. 1 [$y \perp$ (TTF plane), $z \parallel$ (TTF central C–C bond), and $x \perp y$ and z] the only nonzero one-center spin-orbit matrix elements are $\langle \pi_y | \lambda s_z l_z | \sigma_x \rangle$, as shown in Fig. 1, and $\langle \pi_y | \lambda s_x l_x | \sigma_z \rangle$. The σ_x AO's of a given donor have significant overlaps with acceptor π AO's as shown in Fig. 1. The smaller (donor σ_z)-(acceptor π) overlaps will be neglected.

The acceptor π and donor σ orbitals are too dissimilar energywise to be mixed significantly by the electronic Hamiltonian, except for the mixing imposed on overlapping orbitals by the Pauli exclusion principle. As can be shown by writing the wave functions as antisymmetrized products of all occupied orbitals, this mixing is conveniently calculated by orthogonalizing the acceptor π orbitals to the donor S or Se σ orbitals.[6] Thus, tight-binding approximations[7] to the donor and acceptor conduction-band states are

$$\Pi_k^{(\text{D})} = N^{-1/2} \sum_{\mu=0}^{N-1} \pi_\mu^{(\text{D})} \exp\left(\frac{2\pi i k \mu}{N}\right) , \tag{1a}$$

$$\Pi_{k'}^{(\text{A})} = N^{-1/2} \sum_{\eta=0}^{N-1} \left(\pi_\eta^{(\text{A})} - \sum_{\kappa=\eta-1}^{\eta+1} \sum_{\text{ch}} \langle \sigma_{\kappa \text{ch} x}^{(\text{D})} | \pi_\eta^{(\text{A})} \rangle \sigma_{\kappa \text{ch} x}^{(\text{D})} \right) \exp\left(\frac{2\pi i k' \eta}{N}\right) . \tag{1b}$$

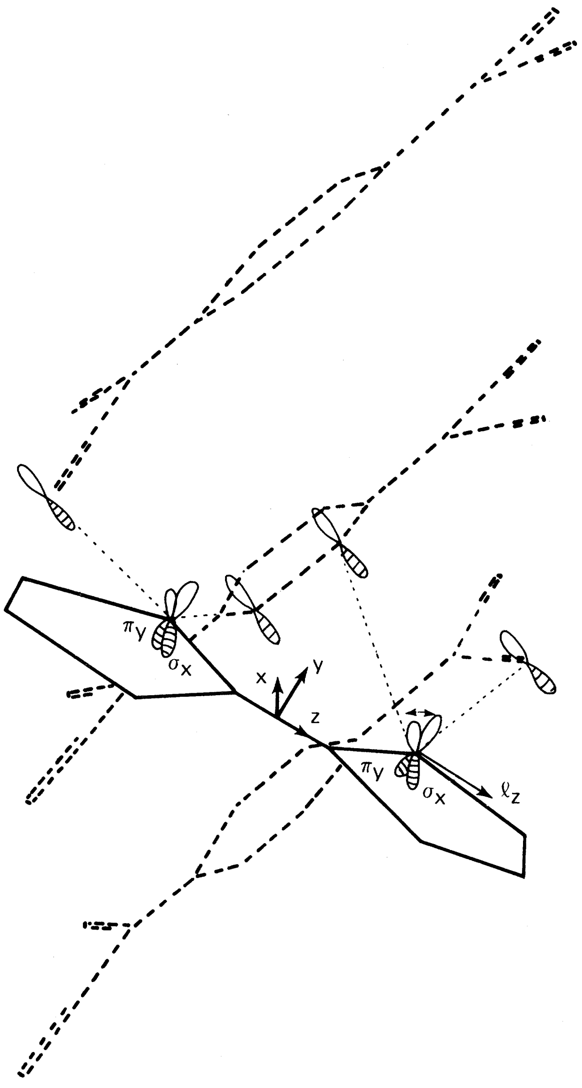

FIG. 1. Effects of spin-orbit interactions and interstack overlap in TTF-TCNQ. Nearest-neighbor overlap pairs are indicated by light dotted lines, but other pairs are included in the calculation. The indicated S-N and S-C pairs are separated by 3.20 and 3.73 Å, respectively.

Here $\pi_\mu^{(D)}$ is the highest occupied π MO of the μth donor molecule, $\pi_\eta^{(A)}$ is the lowest unoccupied MO of the ηth acceptor molecule, and $\sigma_{\kappa \mathrm{ch} x}^{(D)}$ denotes a chalcogen $p\sigma_x$ valence AO on the κth donor molecule. This band model is very approximate because of strong electron-lattice coupling in organic metals such as TTF-TCNQ.[8] It also neglects Coulomb interactions which may explain why ΔH is sometimes independent of the orientation of $\vec{H}$. Nonetheless, this model should provide a reasonable estimate of the spin-orbit coupling because, as will be discussed in more detail later, averaging over the band states largely removes the dependence on details of the band model.

This formalism together with TTF-TCNQ crystal-structure data[4] enables calculation of the spin-orbit matrix elements between Π states of adjoining donor-acceptor stacks. $\pi^{(A)}$ for TCNQ is given by Lowitz.[9] A Hückel MO calculation[10] for TTF, with $\alpha_S = 1.5\beta$ and $\beta_{CS} = 0.8\beta$ ($\alpha_C = 0, \beta_{CC} = \beta$), gives $\rho_S^{1/2} = 0.32$ for all S π AO coefficients in $\pi^{(D)}$. Hartree-Fock AO's[11] were used in the overlap integral calculations. The result is

$$\langle \Pi_{k's'}^{(A)} | H_{\mathrm{ch},z}^{(\mathrm{so})} | \Pi_{ks}^{(D)} \rangle = i\lambda_S \rho_S^{1/2} \langle s' | s_z | s \rangle \delta_{kk'} \times [0.0060 - 0.0137\cos(2\pi k/N)] \,, \tag{2}$$

where $\langle s' | s_z | s \rangle$ is the matrix element for the electron-spin transition which accompanies the interstack transition.

It can be shown that $\langle \Pi_{k's'}^{(D)} | H_{\mathrm{ch},z}^{(\mathrm{so})} | \Pi_{ks}^{(D)} \rangle = 0$ for a donor stack of identical centrosymmetric molecules. Thus, these direct spin-orbit transitions, as contrasted with second-order processes involving electron phonon coupling, do not affect previous conclusions about the ineffectiveness of spin-orbit scattering within a donor stack.[2] To do this we consider the constituent orbital matrix elements: $\langle H_{\mathrm{ch}}^{(O)} \rangle_{\mu\nu} = \langle \pi_\mu^{(D)} | H_{\mathrm{ch}}^{(O)} | \pi_\nu^{(D)} \rangle$ where $\pi_\mu^{(D)}$ and $\pi_\nu^{(D)}$ may contain overlap-admixed $\sigma_\nu^{(D)}$ and $\sigma_\mu^{(D)}$ components, respectively. Since $H_{\mathrm{ch}}^{(O)}$ is Hermitian and imaginary ($\vec{l} = \vec{r} \times \vec{p} = -i\hbar \vec{r} \times \vec{\nabla}$) and the $\pi_\mu^{(D)}$ are real, $\langle H_{\mathrm{ch}}^{(O)} \rangle_{\mu\nu} = -\langle H_{\mathrm{ch}}^{(O)} \rangle_{\nu\mu}$, and $\langle H_{\mathrm{ch}}^{(O)} \rangle_{\mu\mu} = 0$. For centrosymmetric molecules the $\mu\nu$ pair has a symmetry center with $I^{(\mu\nu)} H_{\mathrm{ch}}^{(O)} = H_{\mathrm{ch}}^{(O)}$; $I^{(\mu\nu)} \pi_\mu^{(D)} = \pm \pi_\nu^{(D)}$; and $I^{(\mu\nu)} \pi_\nu^{(D)} = \pm \pi_\mu^{(D)}$ where $I^{(\mu\nu)}$ is the corresponding inversion operator. Thus, $I^{(\mu\nu)} \langle H_{\mathrm{ch}}^{(O)} \rangle_{\mu\nu} = \langle H_{\mathrm{ch}}^{(O)} \rangle_{\nu\mu} = -\langle H_{\mathrm{ch}}^{(O)} \rangle_{\mu\nu}$. Since $\langle H_{\mathrm{ch}}^{(O)} \rangle_{\mu\nu}$ changes sign under $I^{(\mu\nu)}$, it and $\langle \Pi_{k's'}^{(D)} | H_{\mathrm{ch},z}^{(\mathrm{so})} | \Pi_{ks}^{(D)} \rangle$ must vanish. This result, which also holds for interstack spin-orbit coupling between stacks of identically oriented donor molecules, is significant for one-stack materials such as $(\mathrm{TMTSeF})_2X$.[12] Possibly, symmetry-breaking molecular oscillations are involved in the ΔH mechanism in these materials. This would be consistent with observations that $\Delta H[(\mathrm{TMTSeF})_2X]$ is always considerably less than ΔH(TSeF-TCNQ) and, unlike ΔH(TSeF-TCNQ), increases rapidly with increasing temperature.[12] Moreover, the marked increase of ΔH in $(\mathrm{TMTSeF})_2\mathrm{PF}_6$ upon doping with $(\mathrm{TMTTF})_2\mathrm{PF}_6$ may be due to impurity-induced symmetry breaking.[13]

The spin-orbit induced interstack transition rate is[14]

$$W_{ks',ks} = 2\hbar^{-2} |\langle \Pi_{ks'}^{(A)} | H_{\mathrm{ch},z}^{(\mathrm{so})} | \Pi_{ks}^{(D)} \rangle|^2 \tau_{\parallel} / (1 + \tfrac{1}{4}\omega_k^2 \tau_{\parallel}^2) \,, \tag{3}$$

where a factor of 2 is included because each donor electron can go to two acceptor stacks and vice versa, $\hbar\omega_k$ is the transition energy, and $2\tau_{\parallel}^{-1} = \tau_{\parallel A}^{-1} + \tau_{\parallel D}^{-1}$ is the coherence-loss rate in $\langle \Pi_{ks'}^{(A)} | H_{ch,z}^{(so)} | \Pi_{ks}^{(D)} \rangle$ due to intrastack conduction electron scattering at rates $\tau_{\parallel A}^{-1}$ and $\tau_{\parallel D}^{-1}$ for the acceptor and donor stacks.

To estimate ΔH in TTF-TCNQ we first assume that a sufficiently wide range of k states is populated that Eqs. (2) and (3) may be averaged over all k values, i.e., $0 \leqslant k \leqslant N-1$. Second, we assume that $\omega_k \leqslant 2/\tau_{\parallel}$ and hence $\tau_{\parallel}/(1+\frac{1}{4}\omega_k^2\tau_{\parallel}^2) \simeq \tau_{\parallel}$ for most interstack transitions. These assumptions are reasonable first because the energy uncertainty associated with the rapid intrastack electron scattering ($\hbar/\tau_{\parallel} \simeq 0.22$ eV at 300 K, 0.15 eV at 100 K)[8] is comparable to the narrow conduction-band width ($\simeq 0.32$ to 0.55 eV),[15] and, second, the incomplete electron transfer in TTF-TCNQ (charge formula $\mathrm{TTF}^{+0.59}\mathrm{TCNQ}^{-0.59}$)[16] indicates considerable energy overlap between the TTF and TCNQ states. [Because this procedure involves a sum over a complete set of states it is independent of the model used, e.g., the tight-binding model of Eq. (1), to construct the conduction-band functions from the individual π MO's. A rather unrealistic nonband model involving transitions between individual donor-acceptor pairs yields the same result.] With these approximations, and taking $\langle s' | s_z | s \rangle = \frac{1}{2}$, temporarily neglecting its possible angular dependence on $\vec{\mathrm{H}}$, Eqs. (2) and (3) yield for TTF-TCNQ

$$W = \langle W_{ks',ks} \rangle \simeq 6.5 \times 10^{-5} \rho_S (\lambda_S/\hbar)^2 \pi \tau_{\parallel} \simeq 1.0 \times 10^{8}\ \mathrm{sec}^{-1} \qquad (4)$$

for $\rho_S = 0.1$, $\lambda_S/\hbar = 7.2 \times 10^{13}$ sec^{-1},[5] and $\tau_{\parallel} = 3 \times 10^{-15}$ sec^{-1} at 300 K as determined from reflectance spectra[8] which should adequately represent the combined scattering from both stacks. The corresponding ESR line broadening from the uncertainty principle ($\Delta E = \hbar W$) is, in magnetic field units, $\Delta H = 6$ G, in agreement with the observed 6 G at 300 K.[1]

This calculation is readily extended to TSeF-TCNQ. Assuming its crystal structure is identical to that of TTF-TCNQ (they are very similar),[17] and using a Hartree-Fock Se $4p$ AO,[11] yields 0.0072 and −0.0150 for the constant and $\cos(2\pi k/N)$ coefficients, respectively, in Eq. (2). A Hückel MO calculation for TSeF with $\alpha_{Se} = 0.5\beta$ and $\beta_{CSe} = 0.5\beta$,[18] gives $\rho_{Se}^{1/2} = 0.40$. With $\lambda_{Se}/\hbar = 3.8 \times 10^{14}$ sec^{-1},[5] and $\tau_{\parallel} = 4.2 \times 10^{-15}$ sec at 300 K,[17] Eqs. (2)−(5) yield $\Delta H = 452$ G in agreement with the observed 500 G at 300 K.[1] The increase in ΔH on going from TTF-TCNQ to TSeF-TCNQ is largely due to the increased spin-orbit interaction, but an increased unpaired electron density on the less electronegative Se, and a longer $\tau_{\parallel}$ also contribute.

As previously predicted by a dimensionally restricted isotropic metal model,[2(b),19] combination of Eq. (4) with the assumption that $\sigma_{\parallel}^{sp} \propto \tau_{\parallel}$ where $\sigma_{\parallel}^{sp}$ is the single-particle conductivity,[19] predicts: $\Delta H \propto \sigma_{\parallel}^{sp}$. This relation holds for variations of ΔH and $\sigma_{\parallel}^{sp}$ with substance, temperature, and pressure in several TTF-TCNQ–like compounds.[19] It fails in other cases, however, such as TMTTF-TCNQ where ΔH is quite small and has a low-temperature ($T = 40$ K) minimum[1] rather than increasing with $\tau_{\parallel}$ and $\sigma_{\parallel}^{sp}$ as T decreases. Since the TMTTF-TCNQ crystal structure[20] suggests exceptionally weak interstack interactions, its small ΔH may be partly due to molecular-oscillation-induced intradonor stack transitions. This could yield the observed ΔH vs T behavior.

Although the agreement between theory and experiment strongly supports the proposed model, there remains the interesting question of why ΔH is often unexpectedly independent of field orientation.[1] For example, the transitions (D : A ·) ⟷ (D · A :) and (D · A) ⟷ (D A ·), where the dots denote electrons, are (doublet) ⟷ (doublet) spin transitions. They contribute to ΔH only if an electron-spin flip occurs, and thus depend strongly on the orientation of $\vec{\mathrm{H}}$ since $\langle \pm\frac{1}{2} | s_z | \mp\frac{1}{2} \rangle = 0$ unless $\vec{\mathrm{H}} \perp z$.

The transitions (D : A) ⟷ (D· A·) ⟷ (D A:), however, are (singlet) ⟷ (random singlet-triplet pair) spin transitions. The doubly occupied levels must be singlets ($|S\rangle$), and the donor-acceptor pair has a random or uncorrelated spin state [$|RP\rangle = \frac{1}{2} \times \sum_{\xi} \exp(i\chi_{\xi}) |\xi\rangle$ where $\xi = S, T_{-1}, T_0, T_1$ and the ξ's are random-phase angles] because the rapid intrastack scattering makes the lifetime of such a pair in specific states too short for development of a coherent spin state, i.e., the pair is similar to doublet molecules colliding in a fluid. Averaging over the χ's, which eliminates cross terms, and noting that $\sum_{\xi}$ is a complete sum over pair spin states and that s_z operates on only one electron of the pair shows that $|\langle S | s_z | RP \rangle|^2 = \frac{1}{4} \langle S | s_z^2 | S \rangle = \frac{1}{16}$ which result, and thus ΔH, are independent of $\vec{\mathrm{H}}$. (The value $\frac{1}{16}$ is equivalent to $|\langle D | s_z | D \rangle|^2 = \frac{1}{4}$ for doublet transitions because two electrons are relaxed in the pair transition and each has a spin-orbit term.)

A rough estimate of the net spin transition rate, assuming simple band states populated in accordance with the charge formula[16] $\mathrm{TTF}^{+0.59}$-$\mathrm{TCNQ}^{-0.59}$, yields $\Delta H_{\max}/\Delta H_{\min} = 2$ versus the observed 1.2,[1] for angular variation of $\vec{\mathrm{H}}$ in the ac crystal plane. A possible explanation lies in the effect of Coulomb interactions on the band states which, in the valence-bond–like model of Torrance,[21] cause band states formed from basis states with only one electron on a given acceptor molecule (or hole for donor molecules) to be lower in energy than band states formed from basis states with two electrons (or holes) on a given molecule. [The true situation of course lies between the extremes of this and the molecular-orbital model of Eq. (1).] Transitions involving a doubly occupied acceptor state or a doubly vacant donor state will be suppressed if this energy difference is sufficient to yield $\omega_k \geqslant 2/\tau_{\parallel}$ in Eq. (3). For $\tau_{\parallel}=3\times10^{-15}$ sec the required Coulomb contribution to $\hbar\omega_k$ is roughly 0.5 eV, which is similar to other estimates of the Coulomb energy.[21] The only nonsuppressed transition is $(\mathrm{D}{:}\,\mathrm{A}) \leftrightarrow (\mathrm{D}\cdot\mathrm{A}\cdot)$ which is independent of field orientation and is the transition involved in forming the charge-transfer salt.

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