Adiabatic and nonadiabatic electron–intramolecular-vibration couplings and superconductivity in fullerenes

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We have studied adiabatic and nonadiabatic electron–intramolecular-vibration (e-MV) couplings in doped C_{60}. We have shown that nonadiabatic e-MV couplings in the multiband system bring about an interband pair transfer interaction to give T_c enhancement. We have estimated the adiabatic and the nonadiabatic e-MV coupling constants of the doped C_{60}. The dimensionless adiabatic e-MV coupling constants with the lowest three h_g modes are large (0.2–0.4) and they dominate the e-MV couplings in doped C_{60}. The dimensionless nonadiabatic e-MV coupling constants of h_g modes are estimated to be 0.02–0.12. They cannot be neglected in quantitative arguments. The nonadiabatic e-MV coupling may be important even in qualitative arguments of the mechanism of superconductivity if (i) the interband interaction is enhanced by many-body effects and/or if (ii) the nonadiabatic e-MV coupling of A_3C_{60} is larger by a factor of 2 or 3 than that of the dilute limit which we have estimated.

The fullerene superconductors[1] have interesting characteristics such as their strong molecularity even in the solid phase and their nearly degenerate overlapping band structure.[2] These characteristics suggest that intramolecular interactions in the C_{60} molecule are essential to the superconducting mechanism and that dynamic and/or static Jahn-Teller (JT) effects may play an important role.[3–6] It seems that there is a consensus that electron–intramolecular-vibration (e-MV) couplings[3,5,7–9] are important in the mechanism of superconductivity.

On the other hand, it is known that there is a T_c enhancement in overlapping band systems through the interband pair transfer interaction. The interband interaction was first studied by Suhl, Matthias, and Walker and Kondo to explain the T_c enhancement in transition-metal superconductors.[10,11] The interband interaction of Suhl, Matthias, and Walker was assumed to be attractive, but the interband interaction of Kondo is repulsive, originating from an electronic interaction. However, a relation between the interband pair transfer interaction and the nonadiabatic electron–intramolecular-vibration (e-MV) coupling which will be discussed here has not been noticed. Cluster calculations on cuprate superconductors

suggest that there may be nearly overlapping bands consisting of two different combinations of oxygen $2p$ orbitals.[12,13] In this context, the effect of the pair transfer interaction in the cuprate superconductors has been studied by mean-field,[14] random-phase approximation,[15] Lanczos,[16] and quantum Monte Carlo methods.[17] The latest result is that there is a superconducting parameter region even when there is large on-site Coulomb repulsion at the copper site.[17]

After the submission of the original version of this manuscript, Rice, Choi, and Wang published a paper that pointed out the importance of the interband pair transfer interaction in doped C_{60}, but they did not discuss the microscopic origin of this interaction.[18] We have suggested that nonadiabatic e-MV coupling, which is important in JT systems like doped C_{60}, brings about the interband pair transfer interaction.[17] Here we will discuss the nonadiabatic e-MV coupling mechanism of superconductivity in fullerenes and its relevance through estimations of adiabatic and nonadiabatic e-MV coupling constants.

The total Hamiltonian of a multiband system coupled with an intramolecular vibration may be written in the tight-binding approximation as follows:

$$H = \sum_{i=1}^{n}\sum_{l,\sigma}|\phi_{il\sigma}\rangle\varepsilon_l^i\langle\phi_{il\sigma}| + \sum_{i=1}^{n}\sum_{l\neq m,\sigma}|\phi_{il\sigma}\rangle t_{lm}^i\langle\phi_{im\sigma}| + \frac{1}{4}\sum_{i,j}\sum_{l,\sigma}\left[|\phi_{il\sigma}\rangle\left\{\Delta^{ij} + i\kappa^{ij}\left(i\frac{\partial}{\partial Q}\right)\right\}\langle\phi_{jl\sigma}| + \text{H.c.}\right] - \frac{1}{2}\frac{\partial^2}{\partial Q^2} + V, \quad (1)$$

where ε_l^i and t_{lm}^i are the site energy of t_{1u} orbital ϕ_{il} of the C_{60} molecule and the transfer integral between two t_{1u} orbitals of the neighboring C_{60} molecules ϕ_{il} and ϕ_{im}, respectively. Q and V are the normal coordinate of an intramolecular vibration of C_{60} and the Coulomb repulsion between nuclei, respectively.

$$\Delta_l^{ij} = -\langle\phi_{il\sigma}|(\partial^2/\partial Q^2)\phi_{jl\sigma}\rangle, \quad i\kappa_l^{ij} = i\langle\phi_{il\sigma}|(\partial/\partial Q)\phi_{jl\sigma}\rangle$$

come from the nonadiabatic coupling between the conduction electrons and an intramolecular vibration. They are

neglected in the Born-Oppenheimer approximation. The Hamiltonian given by Eq. (1) is equivalent with Born's equation.[19] The nonadiabatic coupling expressed by the third and fourth terms of Eq. (1) is familiar in quantum chemistry.[20,21] Those methods are limited to nondegenerate electronic ground-state molecules with no low-lying excited states and are irrelevant to JT systems. Using a second-quantization expression and expanding ε_l^i in terms of Q, $\varepsilon_l^i \approx \varepsilon_l^i|_0 + \partial\varepsilon_l^i/\partial Q|_0 Q + \frac{1}{2}\partial^2\varepsilon_l^i/\partial Q^2|_0 Q^2$, we have the Hamiltonian for the multiband system coupled with an intramolecular vibration:

$$H = \sum_{i=1}^{n}\sum_{l}\bar{\varepsilon}_l^i n_l^i + \sum_{i=1}^{n}\sum_{l\neq m,\sigma} t_{lm}^i c_{il\sigma}^\dagger c_{im\sigma} + \sum_{i=1}^{n}\sum_{l} U_l^i n_{l\uparrow}^i n_{l\downarrow}^i + \sum_{i=1}^{n}\sum_{l}\bar{g}_l^i n_l^i (b_l + b_l^\dagger) + \sum_{l}\omega_l(b_l^\dagger b_l + \tfrac{1}{2})$$

$$+ \frac{1}{4}\sum_{i,j}\sum_{l,\sigma}(\Delta_l^{ij} c_{il\sigma}^\dagger c_{jl\sigma} + \text{H.c.}) + \frac{1}{4}\sum_{i,j}\sum_{l,\sigma}\{i\bar{\kappa}_l^{ij} c_{il\sigma}^\dagger c_{jl\sigma}i(b_l - b_l^\dagger) + \text{H.c.}\}, \tag{2}$$

where $\bar{\varepsilon}_l^i \approx \varepsilon_l^i|_0$, $\bar{g}_l^i = [1/(2\omega_l)^{1/2}]\partial\varepsilon_l^i/\partial Q|_0$, and $i\bar{\kappa}_l^{ij} = i\kappa_l^{ij}(\omega_l/2)^{1/2}$. $c_{il\sigma}^\dagger$ creates an electron in the ith molecular orbital at the lth site. $b_l^\dagger$ is the creation operator of a boson at lth site. ω_l and U_l^i are the normal-mode frequency of intramolecular vibration at lth site and on-site Coulomb repulsion in the ith molecular orbital at lth site. The on-site Coulomb repulsions are added here to keep generality. The fourth term of Eq. (2) represents deformation-potential-type adiabatic e-MV coupling and it is usually called the Holstein coupling.[22] We ignore the sixth term of Eq. (2), because Δ_l^{ij} will be much smaller than κ_l^{ij}. The seventh term of Eq. (2) represents a novel nonadiabatic e-MV coupling which mixes two bands through coupling with intramolecular vibration. It should be noted that $\bar{\kappa}^{12} = -\bar{\kappa}^{21}$.

The coupling constant $i\bar{\kappa}_l^{ij}$ can be formally expressed as follows:

$$i\bar{\kappa}_l^{ij} = i(\omega_l/2)^{1/2}\langle\phi_{il\sigma}|(\partial h/\partial Q)|\phi_{jl\sigma}\rangle/(\varepsilon_l^j - \varepsilon_l^i), \tag{3}$$

where h is the single-particle effective Hamiltonian.

We expect larger nonadiabatic coupling when the orbital energy difference is small. There is a reduction of the nonadiabatic effect in the antiadiabatic regime: $|\varepsilon_l^j - \varepsilon_l^i| \sim 0$.[23] The reduction effect can be seen in this narrow parameter region. The nonadiabatic effect is unreduced when $|\varepsilon_l^j - \varepsilon_l^i| \sim \omega$; this is the case of doped C_{60}.[24] There is no diagonal nonadiabatic e-MV coupling. There are no on-site off-diagonal electronic terms coupled with phonons in the molecule, because we used adiabatic electronic configuration functions in the Born expansion. Using the standard canonical transformation technique, we obtain the following effective Hamiltonian which includes an intraband BCS-type attractive interaction and the interband pair transfer interaction which is repulsive within the cutoff energy:

$$\tilde{H} = \sum_{i=1}^{n}\tilde{\varepsilon}_{k\sigma}^i c_{ik\sigma}^\dagger c_{ik\sigma} + \sum_{\langle i,j\rangle}\sum_{k,k'}K_{ij}(k,k')(c_{ik\uparrow}^\dagger c_{i-k\downarrow}^\dagger c_{j-k'\downarrow}c_{jk'\uparrow} + \text{H.c.}) - \sum_{\langle i,j\rangle}\sum_{k,k',\sigma,\sigma'}J_{ij}(k,k')(c_{ik\sigma}^\dagger c_{i-k\sigma'}c_{j-k'\sigma'}^\dagger c_{jk'\sigma} + \text{H.c.})$$

$$+ \frac{1}{2}\sum_{i,k,k'}W_i(k,k')(c_{ik\uparrow}^\dagger c_{i-k\downarrow}^\dagger c_{i-k'\downarrow}c_{ik'\uparrow} + \text{H.c.}), \tag{4}$$

where $K_{ij}(k,k') = [K\Theta_i(k)\Theta_j(k') + K_{ij}]/N$, $J_{ij}(k,k') = [J\Theta_i(k)\Theta_j(k') + J_{ij}]/N$, $W_i(k,k') = [-V_i\Theta_i(k)\times\Theta_i(k') + U]/N$. $\Theta(k)$ is the cutoff function. We have included the electronic terms K_{ij}, J_{ij}, and U, to keep the generality of Eq. (4). These are respectively the exchangelike integral which represents the strength of Kondo-type interband pair transfer interaction of electronic origin, exchange integral, and on-site Coulomb repulsion. These electronic terms may be very small in doped C_{60} and we neglect K_{ij} and J_{ij}. The third term of Eq. (4) represents exchange interaction between the two bands which is brought about by the nonadiabatic e-MV coupling. This term vanishes in the mean-field and random-phase approximations, so we ignore this term at present. The interband and intraband potentials K and V are given as follows:

$$K = \bar{\kappa}^2/4\omega, \quad V = 2\bar{g}^2/\omega. \tag{5}$$

It should be noted that there are no interband electronic interactions originating from other than the seventh term of Eq. (2) in our formulation where the adiabatic electronic wave functions rather than the diabatic electronic wave functions are used as basis functions. If we assume the two bands i and j are identical, the dimensionless coupling constant involved in the McMillan-type formula for T_c is given simply by $\lambda_{\text{nonad}} = N(0)K$ and $\lambda_{\text{ad}} = N(0)V$ for the nonadiabatic and adiabatic e-MV couplings, respectively.[12] $N(0)$ is the density of states at the Fermi level. An expression for T_c in this case is given as follows within the mean-field theory:[14]

$$T_c = 1.13\omega\exp[-1/(\lambda - \mu^*)], \tag{6}$$

where $\lambda = \lambda_{\text{ad}} + \lambda_{\text{nonad}}$ and μ^* is the screened Coulomb interaction. We estimate λ_{nonad} and λ_{ad} through the calculation of $\bar{\kappa}$ and $\bar{g}$ in the C_{60}^- anion.

To estimate the adiabatic and nonadiabatic e-MV coupling constants $\bar{\kappa}$ and $\bar{g}$ in the doped C_{60}, we have done molecular-orbital calculations of C_{60}^-. We have optimized the structure of this anion and have also done a normal-coordinate analysis. We have estimated the coupling constants in this anion with distorted geometry and some vibrational modes which have largest overlap with the h_g and a_g modes of C_{60}. Taking into account of the remarkable molecularity even after doping, we expect that our estimation is helpful to understand the e-MV couplings in the doped C_{60}. We have adopted the modified neglect of differential overlap approximation[25,26] proposed by Dewar and Thiel throughout this paper. A 3×3 configuration interaction has been done with a reference configuration obtained by "half-electron" approximation[27] introduced for open-shell systems by Dewar, Hashmall, and Venier. The structural optimizations and normal-coordinate analyses have been done on the energy surface obtained by the 3×3 configuration interaction for C_{60}^- and by a Hartree-Fock calculation for C_{60}, respectively. The optimized bond lengths and vibrational frequencies of C_{60} agree with the published results.[28,29]

When an electron is attached, the equilibrium structure of C_{60} becomes unstable and the C_{60}^- anion distorts in a classical sense. We have done a full optimization of the stable structure of C_{60}^-. The triple degeneracy of the t_{1u} orbitals is partly lifted at the optimized structure (one occupied orbital and two unoccupied orbitals which are degenerate), which is consistent with the results obtained by

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TABLE I. Calculated frequency shifts $\Delta\omega = \omega_{C_{60}(-)} - \omega_{C_{60}}$ and principal components of normal mode vectors of C_{60}^- and their relative weights (in percent).

	v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8	v_9	v_{10}
$\Delta\omega$	1.4	5	0.6	−1.2	2.1	2.3	1.9	−11.0	−16.4	−13.0
Modes	$h_g(1)$	$h_g(2)$	$a_g(1)$	$h_g(3)$	$h_g(4)$	$h_g(5)$	$h_g(6)$	$h_g(7)$	$a_g(2)$	$h_g(8)$
	100%	98%	100%	96%	99%	99%	79%	99%	99%	99%

the extended Su-Schrieffer-Heeger model.[30−32] The split-off energy is calculated to be 0.09 eV. A JT stabilization energy defined as the total energy difference between optimized C_{60}^- and undistorted C_{60}^- is calculated to be 0.052 eV (419 cm^{-1}), which is larger than a zero-point vibrational energy of the lowest h_g mode of C_{60} (263 cm^{-1}), but is smaller than that of the higher frequency h_g and a_g modes (1600–1720 cm^{-1}). It is difficult to conclude whether the static distortions are really observable or not. However, it is clear that there is a dynamic JT effect in this anion.

A normal-coordinate analysis of C_{60}^- at the optimized distorted structure was done. To investigate the nature of the intramolecular vibrations of the anion, the normal modes of C_{60}^- are expanded by the modes of C_{60}. The results are summarized in Table I. It should be noted that the frequency shifts of the highest two h_g modes and the highest a_g modes of C_{60}, which have large contributions to the static JT distortion, are large. The three modes soften upon doping by 11–16 cm^{-1}. A Raman experiment[8] reports that there is a shift by 11 cm^{-1} of the highest a_g mode, whose intensity remains very large upon Rb and K doping. The shift may be a consequence of the static JT distortion.

We estimate $\bar{\kappa}$, K, and λ_{nonad} defined between the singly occupied molecular orbital (SOMO) and one of the lowest unoccupied molecular orbitals (LUMOs) of C_{60}^-. We estimate $\tilde{g}$, V, and λ_{ad} defined on the SOMO of C_{60}^-. Realistic estimation of the coupling constants of C_{60}^{3-} is difficult technically. We believe our estimated coupling constants in the dilute limit have some implications for those of A_3C_{60}. $\bar{\kappa}$ and $\tilde{g}$ are calculated numerically. The results are tabulated in Table II. We have chosen ten normal vibrations of C_{60}^-, whose characteristics are summarized in Table I. $\bar{\kappa}$, $\tilde{g}$, and ω of the v_{10} mode (correspond-

ing to the highest h_g mode of C_{60}) are −0.05, 0.03, and 0.21 eV, respectively. K and V are 3.17 and 8.69 meV, respectively. We estimate λ_{nonad} and λ_{ad} to be 0.06 and 0.17, where we have assumed the frequently used value $N(0) = 20$ states/eV per spin C_{60}. Taking into account that there is another LUMO (doubly degenerate) that contributes to the interband mixing, λ_{nonad} may be multiplied by the factor 2. The dimensionless nonadiabatic e-MV coupling constant with this mode is smaller by a factor of 1.4 compared with that of adiabatic e-MV coupling only. The adiabatic e-MV couplings with the lowest three h_g modes (v_1, v_2, and v_4) are very large (λ_{ad} = 0.2–0.4). These couplings dominate the electron-intramolecular-vibration couplings in this anion. This is roughly in agreement with a recent Raman experiment[9] which has reported that the e-MV coupling with the second lowest h_g mode is important. The nonadiabatic e-MV coupling constants ($2\lambda_{nonad}$) of h_g modes are estimated to be 0.02–0.12. There still is a chance that the nonadiabatic e-MV couplings play not only a qualitatively but also quantitatively important role in the mechanism of superconductivity in the doped fullerenes if (i) the interband scattering is enhanced by many-body effects beyond the mean-field prediction given by Eq. (6), and/or if (ii) the nonadiabatic e-MV coupling of C_{60}^{3-} is larger than that of C_{60}^- by a factor of 2 or 3. The ladder and the bubble diagrams have been analyzed in a related model with two-body interband pair transfer interactions by Yamaji.[15] He obtained divergent enhancement of the electronic interactions. It is not impossible that the coupling constants of C_{60}^{3-} are larger than that of C_{60}^-, because we expect that $|\varepsilon_i^j - \varepsilon_i^j| \sim \omega$ in A_3C_{60}. These issues should be clarified later. Recent Raman and neutron experiments suggest that the highest h_g mode is strongly coupled with electrons. Our result indicates that the nonadiabatic e-MV

TABLE II. Frequencies of C_{60}^-, calculated e-MV coupling constants $\bar{\kappa}$ and $\tilde{g}$ (eV), the pair transfer integral K (meV), the BCS attractive potential V (meV), and the dimensionless e-MV coupling constants λ_{nonad} and λ_{ad} of C_{60}^-. λ_{nonad} is doubled ($2\lambda_{nonad}$) to include a contribution from another LUMO. We use the parameter $N(0) = 20$ states/eV per spin C_{60}. The numbering of vibrational modes is the same as that in Table I.

	v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8	v_9	v_{10}
$\omega_{C_{60}^-}$	264	452	611	770	926	1262	1408	1585	1661	1709
$\bar{\kappa}$	0.00	−0.01	−0.01	−0.03	0.02	0.03	−0.03	−0.02	0.02	−0.05
$\tilde{g}$	0.02	0.02	0.01	−0.03	−0.02	0.02	−0.01	0.02	0.01	0.03
K	0.00	0.39	0.37	2.33	0.75	1.45	0.91	0.70	0.50	3.17
V	18.4	10.9	5.56	19.6	4.05	4.81	1.78	3.82	1.05	8.69
λ_{nonad}	0.00	0.01	0.01	0.05	0.01	0.03	0.02	0.01	0.01	0.06
$2\lambda_{nonad}$	0.00	0.02	0.02	0.10	0.02	0.06	0.04	0.02	0.02	0.12
λ_{ad}	0.37	0.22	0.11	0.39	0.08	0.10	0.04	0.08	0.02	0.17

coupling in addition to the adiabatic e-MV coupling is large with this mode. The λ_{ad} has already been estimated by other groups.[3,5] Varma, Zaanen, and Raghavachari concluded that λ_{ad} is largest with the second highest h_g mode (v_8) and that the coupling constants with the lowest three h_g modes $(v_1, v_2,$ and $v_4)$ are relatively small compared with the second highest h_g mode.[5] Our $\partial\varepsilon/\partial Q|_0$ with the lowest three h_g modes are larger than those of Ref. 5. It is not clear why their results on the adiabatic e-MV coupling constants are different from ours, though they used the similar quantum chemical methods that we have adopted. Schlüter $et\ al.$[3] have also estimated λ_{ad} for h_g and a_g modes using the local-density approximation method. Their result is qualitatively in agreement with ours. Quite recently, they have also discussed an enhancement of T_c due to the dynamic JT effect.[33] Their result is closely related with our result on the nonadiabatic e-MV coupling, though the results are obtained with different basis representations.

The nonadiabatic e-MV coupling of tetrathiafulvalene molecule[34] is at least 10–100 (for the most vibrational modes of TTF, more than 1000) times smaller than that of $C_{60}{}^-$. The BCS potential V of the doped C_{60} is somewhat smaller than that of organic superconductors composed of TTF analogs,[22,35] but the dimensionless adiabatic e-MV coupling constant of the doped C_{60} is larger than that of organic superconductors composed of TTF analogs due to the large density of states at the Fermi level. These facts may have some relation with the unexpectedly high transition temperature of the doped fullereness among organic superconductors.

To summarize, we have studied the adiabatic and nonadiabatic electron–intramolecular-vibration couplings in an overlapping multiband system: doped C_{60}. We have shown that the nonadiabatic e-MV coupling in this system brings about an interband pair transfer interaction to give T_c enhancement. We have estimated the coupling constants of adiabatic and nonadiabatic e-MV couplings. We conclude that the adiabatic e-MV coupling constants with the lowest three h_g modes are dominant but the contributions from the nonadiabatic e-MV couplings cannot be neglected at least quantitatively in the mechanism of superconductivity in the doped C_{60}.

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