Jahn-Teller mechanism of the half width of the intramolecular vibrational spectrum in doped C_{60}: Coupling with H_g, T_{1u}, and H_u modes

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We have studied the half width of the intramolecular vibrational spectrum of the nonadiabatic electron intramolecular vibration (*e*-MV) coupling origin in doped C_{60}. We have also estimated the half width of the adiabatic *e*-MV coupling origin. We found that along with the two *e*-MV couplings with H_g modes, there are some modes with H_u and T_{1u} symmetries that couple with conduction electrons and may have non-negligible phonon widths. This mainly comes from a local symmetry reduction due to the Jahn-Teller distortion. The theoretical results agree with previous experimental results with H_g modes and may agree qualitatively with recent experimental findings for the H_u and T_{1u} modes. Our *e*-MV theory based on Jahn-Teller effects explains most of the experimental observations related to the half width of the phonon spectrum in doped C_{60}. We predict a doping-induced structure for the highest frequency H_g mode, which comes from the large coupling constants of both the adiabatic and the nonadiabatic *e*-MV mode coupling.

I. INTRODUCTION

The superconductivity found in A_xC_{60} has stimulated studies of electron intramolecular vibration (*e*-MV) couplings in solids.[1] Among them, intramolecular Jahn-Teller (JT) effects have received much attention.[2,3] Inelastic neutron scattering measurements[4,5] and Raman scattering measurements[6,7] supplied important information about *e*-MV coupling strengths. These measurements showed that the low-frequency tangential H_g modes contribute about as much as the higher-frequency radial H_g mode. This tendency agrees with some of the common features of previous theoretical results,[8–11] which were obtained using different theoretical methods. Besides these results, the ^{13}C isotope effect on T_c, measured by some groups, supports the idea that there are large contributions of phonons in the mechanism of superconductivity.[12–16] These results put constraints on some models, which rely entirely on hypothetical magnetic fluctuation in doped C_{60}.[17] Recent photoemission results exclude the possibility of the formation of the pseudogap in K_3C_{60}.[18] The other important experimental results obtained recently are the giant vibrational resonance of T_{1u} modes found in optical measurements[19,20] and the broadenings of H_u and T_{1u} modes upon doping found in an inelastic neutron scattering experiment.[21] The giant vibrational resonance was studied phenomenologically by Rice and Choi.[22] We report here that our *e*-MV theory including both the adiabatic and the nonadiabatic *e*-MV couplings[10] explains experimental observations related to phonon spectrum broadenings qualitatively and that the broadenings observed with some H_u and T_{1u} modes may originate entirely from the JT mechanism.

In Sec. II we show rigorously the existence of the nonadiabatic *e*-MV coupling term. In doped C_{60} the nonadiabatic *e*-MV coupling term gives leading contributions to the noadiabatic correction to the phonon self-energy than that from higher-order terms with the adiabatic *e*-MV coupling beyond the Migdal approximation. In Sec. III we present formulas of the lowest-order phonon self-energy and half width of the phonon spectrum of a nonadiabatic *e*-MV origin. In Sec. IV we estimate the width of the H_g, A_g, H_u, T_{1u}, and A_u modes of doped C_{60} with both the adiabatic and the nonadiabatic *e*-MV coupling terms.

II. NONADIABATIC *e*-MV COUPLING TERM

We show rigorously that there exists a nonadiabatic *e*-MV coupling correction term to the Born-Oppenheimer (BO) adiabatic approximation. In the most rigorous meaning, the correction term cannot be neglected when one uses the BO adiabatic electronic wave function. We may expect that the nonadiabatic *e*-MV coupling coefficients may be small enough to be neglected in many materials; however, these coefficients are large in doped C_{60} and they cannot be neglected.

We start with the following molecular Hamiltonian:

$$H=\frac{p^2}{M}+V(q)+\int a^+(1)h(1,q)a(1)d(1)+\frac{1}{2}\int\int a^+(1)a^+(2)\frac{e^2}{r_{12}}a(2)a(1)d(1)d(2)\,, \quad (1)$$

where q, p, and M are the normal coordinates of molecular vibration, nuclear momentum, and nuclear mass, respectively. The variables 1 and 2 denote the coordinates of the electrons including the spin variables. $h(1,q)$ denotes the one-body term for the electrons and e^2/r_{12} denotes Coulomb repulsion between them. The annihilation operator $a(1)$ is defined as $a(1)=\sum_j \psi_j(1;q)c_j$, where c_j is the annihilation operator for electrons with orthonormalized molecular orbitals ψ_j. It should be noted that ψ depends on q parametrically. As nuclei and electrons

are independent particles, we need the following commutation relation to hold:

$$[p,a]=0 \ . \tag{2}$$

The parametric dependence of ψ on q due to the BO adiabatic approximation does not allow p and c_j to commute:

$$[p,c_j]=-i\sum_i \left\langle \frac{\partial}{\partial q}\psi_j \middle| \psi_i \right\rangle c_i \ . \tag{3}$$

This noncommutation relation makes calculations in the nonadiabatic problem very complicated. We can remedy this difficulty by introducing the function

$$X(1,2)\equiv\sum_k \frac{\partial}{\partial q}\psi_k(1)\psi_k^*(2) \tag{4}$$

and the recoil momentum operator following Fukutome:[23]

$$\pi\equiv -i\int\int a^+(1)X(1,2)a(2)d(1)d(2) \ . \tag{5}$$

With the help of the relations

$$\int X(1,2)\psi_k(2)d(2)=\frac{\partial}{\partial q}\psi_k(1) \ , \tag{6a}$$

$$\int \psi_k^*(1)X(1,2)d(1)=-\frac{\partial}{\partial q}\psi_l^*(2) \ , \tag{6b}$$

we find the following relation to hold:

$$[\pi,c_j]=[p,c_j] \ . \tag{7}$$

If we define a new nuclear momentum P by

$$P\equiv p-\pi \ , \tag{8}$$

we then observe that

$$[P,c_j]=0 \ , \tag{9}$$

and the commutation relation for P and q is preserved. Now we have a set of canonical variables which have desirable communication relations. With the new nuclear momentum P, the molecular Hamiltonian given by Eq. (1) is rewritten as follows:

$$H=\frac{P^2}{M}+V(q)+\sum_{ij}\langle\psi_i|h|\psi_j\rangle c_i^\dagger c_j+\frac{1}{2}\sum_{ijkl}([il|jk]-\{il|jk\})c_i^\dagger c_j^\dagger c_k c_l+\frac{1}{2}\sum_{ij} i\left\langle\psi_i\middle|\frac{\partial}{\partial Q}\psi_j\right\rangle c_i^\dagger c_j i\sqrt{\omega/2}(b-b^\dagger)$$
$$-\frac{1}{2}\sum_{ij}\left[\left\langle\frac{\partial}{\partial Q}\psi_i\middle|\frac{\partial}{\partial Q}\psi_j\right\rangle+\left\langle\psi_i\middle|\frac{\partial^2}{\partial Q^2}\psi_j\right\rangle\right]c_i^\dagger c_j \ , \tag{10a}$$

$$[ij|kl]=\int\int\psi_i^*(1)\psi_j^*(2)\frac{e^2}{r_{12}}\psi_k(2)\psi_l(2)d(1)d(2) \ , \tag{10b}$$

$$\{ij|kl\}=\left\langle\psi_i\middle|\frac{\partial}{\partial Q}\psi_l\right\rangle\left\langle\frac{\partial}{\partial Q}\psi_k\middle|\psi_j\right\rangle \ , \tag{10c}$$

where Q is the mass-weighted normal coordinate defined by $Q=\sqrt{M}q$ and ω is the molecular vibrational frequency. Equation (10) is the most convenient Hamiltonian to start the nonadiabatic e-MV problem. If one tries to use Eq. (1), one has to deal with the noncommutability of p and c_j as shown in Eq. (3). In the adiabatic limit, where the parametric dependence of ψ on q or Q can be neglected, we may suppose the approximate commutability between p and c_j and neglect terms in the second and third lines of Eq. (10a). In doped C_{60}, we observe, with the help of quantum chemistry, that quantities such as $\langle\psi_i|(\partial/\partial Q)\psi_j\rangle$ can never be negligible, i.e., doped C_{60} is a Jahn-Teller system. On the basis of these arguments, doped C_{60} may be best described by the following model Hamiltonian:

$$H=H_0+H_1 \ , \tag{11a}$$

$$H_1=H_{11}+H_{12} \ , \tag{11b}$$

$$H_0=\sum_{i=1}^n \epsilon_l^i n_l^i+\sum_i^n\sum_{l\neq m,\sigma} t_{lm}^i c_{il\sigma}^\dagger c_{im\sigma}+\sum_l \omega_l(b_l^\dagger b_l+\tfrac{1}{2}) \ , \tag{11c}$$

$$H_{11}=\sum_i^n\sum_l g_l^i n_l^i(b_l+b_l^\dagger) \ , \tag{11d}$$

$$H_{12}=\sum_{\langle ij\rangle}\sum_{l\sigma}\{i\kappa_l^{ij}c_{il\sigma}^\dagger c_{jl\sigma}i(b_l-b_l^\dagger)+\text{H.c.}\} \ , \tag{11e}$$

where $c_{il\sigma}^\dagger$ and $b_l^\dagger$ are creation operators for electrons with spin σ on the lth site of the ith band and of molecular vibrational bosons on the lth site, respectively. ϵ_l^i, t_{lm}^i, g_l^i, and κ_l^{ij} are the site energy of the ith band, the transfer integral of the ith band, the adiabatic e-MV coupling constant of the ith band, and the nonadiabatic e-MV coupling constant between the ith and jth bands, respectively. H_{11} and H_{12} are the adiabatic and the nonadiabatic e-MV couplings.[10] We have used a Taylor expansion with respect to Q to take into account the site energy modulation effect by the phonon. The adiabatic e-MV coupling term comes from this effect and is called Holstein coupling.[24] Long-range interactions such as the long-range transfer interaction are neglected on the basis of the strong molecularity of C_{60}. We have estimated g_l^i and κ_l^{ij} of C_{60}^- and found that these are comparable in magnitude of order 0.01.[10] The higher-order correction to the lowest-order phonon self-energy with the adiabatic e-MV coupling H_{11} is of the order of g^4. The cross term

contribution to the phonon self-energy between the adiabatic e-MV coupling term H_{11} and the nonadiabatic e-MV coupling term H_{12} is of the order of $g^2\kappa^2$.

We neglect these higher-order contributions expecting that the integral associated with the vertex correction to the lowest-order phonon self-energy is not singular (Migdal approximation).[25,26] If the expectation is valid or not depends on the actual values of the parameters and it is very difficult to know if the approximation works or not in doped C_{60}. With the Fermi energy $\epsilon_F=0.9$ eV and the partial density of state of each t_{1u} band $N(0)=2.5$ states/eV C_{60}^- per spin, we may neglect the higher-order corrections. Justifications should be looked at for comparisons with the calculated results and experiments. The bottom line is that there is the lowest-order phonon self-energy with a novel nonadiabatic e-MV coupling whose prefactor is over 10^4 larger than that of the higher-order corrections which have been believed to play an exclusive role in the nonadiabatic effects so far. The effect of the nonadiabatic e-MV coupling has not been understood yet and we think it worthwhile to start with the lowest-order contributions. The lowest-order contribution from the nonadiabatic e-MV coupling is independent of the singularity of the integral associated with the vertex correction.

III. LOWEST-ORDER PHONON SELF-ENERGY WITH NONADIABATIC e-MV COUPLING

We derive formulas of the lowest-order phonon self-energy and the half width of the phonon spectrum with the nonadiabatic e-MV coupling term by use of the standard Feynman diagrammatic technique.[27–29] We define the adiabatic and the nonadiabatic phonon finite temperature Green's functions as follows:

$$D_q^{\rm ad}[\tau,\tau']=-\langle TU_{\rm ad}(\beta)u_q(\tau)u_{-q}(\tau')\rangle_0 , \tag{12a}$$

$$D_q^{\rm nonad}[\tau,\tau']=-\langle TU_{\rm nonad}(\beta)\phi_q(\tau)\phi_{-q}(\tau')\rangle_0 , \tag{12b}$$

$$U_{\rm ad}(\beta)=1+\sum_{n=1}^{\infty}(-1)^n\int_0^{\beta}du_1\int_0^{u_1}du_2\cdots\int_0^{u_{n-1}}H_{11}(u_1)\cdots H_{11}(u_n)du_n , \tag{12c}$$

$$U_{\rm nonad}(\beta)=1+\sum_{n=1}^{\infty}(-1)^n\int_0^{\beta}du_1\int_0^{u_1}du_2\cdots\int_0^{u_n-1}H_{12}(u_1)\cdots H_{12}(u_n)du_n , \tag{12d}$$

where $\langle\cdots\rangle_0=\mathrm{Tr}(\cdots e^{-\beta H_0})/\mathrm{Tr}(e^{-\beta H_0})$, $u_q(\tau)=b_q(\tau)+b_{-q}^{\dagger}(\tau)$, $\phi_q(\tau)=b_q(\tau)-b_{-q}^{\dagger}(\tau)$, and $\beta=1/k_BT$.

We supposed that the cross term between H_{11} and H_{12} is much less smaller than the lowest-order contributions. We may use the following approximate Dyson equation in our system:

$$\mathbf{D}_{\mathbf{q}}(\omega)\simeq\frac{-1}{[\mathbf{D}_{\mathbf{q}}^{(0)}(\omega)]^{-1}-\mathbf{\Pi}^{(2)}(\mathbf{q},\omega)} , \tag{13a}$$

$$\mathbf{D}_{\mathbf{q}}(\omega)=\begin{bmatrix} D_q^{\rm ad}(\omega) & 0 \\ 0 & D_q^{\rm nonad}(\omega)\end{bmatrix} , \tag{13b}$$

$$\mathbf{\Pi}^{(2)}(\mathbf{q},\omega)=\begin{bmatrix} \Pi^{{\rm ad}(2)}(q,\omega) & 0 \\ 0 & \Pi^{{\rm nonad}(2)}(q,\omega)\end{bmatrix} . \tag{13c}$$

This means that frequency shifts and the width of the adiabatic and the nonadiabatic e-MV coupling origins may be approximately independent. The nonadiabatic e-MV coupling gives rise to doping-induced additional fine structure of the phonon spectrum, which might be observed by experiments.

We assume that the ith and jth bands are separated by a constant energy Δ and have the same dispersion, for simplicity: $\epsilon_{j\mathbf{k}}=e_{\mathbf{k}}$, $\epsilon_{i\mathbf{k}}=\Delta+e_{\mathbf{k}}$ and $e_{\mathbf{k}}=k^2/2m$, where m is the effective mass of the band. We neglect the ladder process and use the bare Green's functions to calculate the vertex function and the phonon self-energy. The lowest-order vertex function of the nonadiabatic e-MV coupling in the ground state defined by $\Gamma^{\rm nonad}=\kappa_{ij}(1+\Gamma^{(2){\rm nonad}}+\cdots)$ is estimated as follows:

$$\Gamma^{(2){\rm nonad}}(q,\omega)\sim\sqrt{1/M}\ln\frac{\Delta+qv_F-\omega-i\delta}{\Delta-qv_F-\omega-i\delta} , \tag{14}$$

where v_F is the Fermi velocity. We may neglect the vertex correction to the phonon self-energy. The lowest-order phonon self-energy of the nonadiabatic e-MV coupling origin is given in the normal ground state as follows:

$$\Pi^{(2)\text{nonad}}(q,\omega)=-\sum_{\langle ij\rangle}\kappa_{ij}^2\frac{mk_{Fj}}{2\pi^2}\left[-\frac{1}{2}-\frac{\tilde{\omega}'-\tilde{\Delta}'}{\tilde{q}'^2}+\frac{1}{2\tilde{q}'}\left\{1-\left[\frac{\tilde{\omega}'-\tilde{\Delta}'}{\tilde{q}'}+\frac{\tilde{q}'}{2}\right]^2\right\}\ln\left|\frac{1-\left[\frac{\tilde{\omega}'-\tilde{\Delta}'}{\tilde{q}'}+\frac{\tilde{q}'}{2}\right]}{1+\left[\frac{\tilde{\omega}'-\tilde{\Delta}'}{\tilde{q}'}+\frac{\tilde{q}'}{2}\right]}\right|\right]$$
$$-\sum_{\langle ij\rangle}\kappa_{ij}^2\frac{mk_{Fi}}{2\pi^2}\left[-\frac{1}{2}+\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}^2}-\frac{1}{2\tilde{q}}\left\{1-\left[\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}}-\frac{\tilde{q}}{2}\right]^2\right\}\ln\left|\frac{1-\left[\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}}-\frac{\tilde{q}}{2}\right]}{1+\left[\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}}-\frac{\tilde{q}}{2}\right]}\right|\right]+i\sum_{\langle ij\rangle}\kappa_{ij}^2\frac{m^2\omega}{2\pi q}\ , \tag{15}$$

where $\tilde{\omega}\equiv m\omega/k_{Fi}^2$, $\tilde{q}\equiv q/k_{Fi}$, $\tilde{\Delta}\equiv m\omega/k_{Fi}^2$, $\tilde{\omega}'\equiv m\omega/k_{Fj}^2$, $\tilde{q}'\equiv q/k_{Fj}$, and $\tilde{\Delta}'\equiv m\omega/k_{Fj}^2$. Here we assumed both the ith and jth bands cross the Fermi level. If the band splitting energy Δ is small and $q^2\gg 2m\Delta$, we obtain the following formulas for the frequency shift and the Lorentz half width of intramolecular vibration:

$$\left[\frac{\Delta\omega_{\text{vib}}}{\omega_{\text{vib}}}\right]_{\text{nonad}}=-\frac{1}{2}\lambda_{\text{nonad}}/d\ , \tag{16a}$$

$$\gamma_{\text{nonad}}=\frac{\pi}{2}N(0)\lambda_{\text{nonad}}\omega_{\text{vib}}^2/d\ , \tag{16b}$$

$$\lambda_{\text{nonad}}=N(0)\kappa^2/\omega_{\text{vib}}\ , \tag{16c}$$

where $N(0)$, d, and κ^2 are the partial density of state at the Fermi level per each band, which is supposed to be identical for the ith and jth bands, the degeneracy of the molecular vibrational modes, and the sum of the square of the nonadiabatic e-MV coupling constants over the degenerate vibrational modes, respectively. In the case where the ith band crosses the Fermi level but the jth band does not, the lowest-order phonon self-energy of the nonadiabatic e-MV coupling origin is given as follows:

$$\Pi^{(2)\text{nonad}}(q,\omega)=-\sum_{\langle ij\rangle}\kappa_{ij}^2\frac{mk_{Fi}}{2\pi^2}\left[-\frac{1}{2}+\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}^2}-\frac{1}{2\tilde{q}}\left\{1-\left[\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}}-\frac{\tilde{q}}{2}\right]^2\right\}\ln\left|\frac{1-\left[\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}}-\frac{\tilde{q}}{2}\right]}{1+\left[\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}}-\frac{\tilde{q}}{2}\right]}\right|\right]$$
$$+i\sum_{\langle ij\rangle}\kappa_{ij}^2\frac{mk_{Fi}}{4\pi\tilde{q}}\left[1-\left[\frac{\tilde{\omega}-\tilde{\Delta}}{\tilde{q}}-\frac{\tilde{q}}{2}\right]^2\right]\ . \tag{17}$$

This leads to a very approximate formula of the Lorenzian half width of intramolecular vibration:

$$\gamma_{\text{nonad}}\simeq\frac{\epsilon_F}{\omega_{\text{vib}}}\frac{\pi}{2}N(0)\lambda_{\text{nonad}}\omega_{\text{vib}}^2/d\ , \tag{18}$$

where $\epsilon_F<\Delta\ll 4\epsilon_F$. For solids with strong molecularity like C_{60}, the factor $\epsilon_F/\omega_{\text{vib}}$ may take a value of about 2–20. One can find corresponding formulas for the adiabatic e-MV coupling in the literature.[2,8,30]

IV. HALF WIDTH OF THE PHONON SPECTRUM IN DOPED C_{60}

We calculate the half width of the phonon spectrum of the H_g, A_g, H_u, T_{1u}, and A_u modes in doped C_{60} with both the adiabatic and the nonadiabatic e-MV coupling terms. We have adopted the modified neglect of differential overlap (MNDO) approximation[31] for the molecular electronic wave function to calculate coupling constants with the H_g, A_g, H_u, T_{1u}, and A_u modes using C_{60}^- as a model of A_3C_{60}. The details of the quantum chemical calculation are similar to those in a previous paper.[10] It should be noted that calculations of the e-MV coupling constants appearing in Eq. (11) are done with one of the distorted structures located in a drainlike structure of the potential energy surface (PES) of (a Goldstone-like mode) C_{60}^-.[32] Changes of the C-C bond lengths from the neutral molecule are of order 0.01 Å.[10] The adiabatic e-MV coupling brings about interactions between the H_g and A_g vibrational modes (JT active) and intraband scattering. The nonadiabatic e-MV coupling with the H_g and A_g modes brings about interactions with interband mixing between the t_{1u} derived bands. The nonadiabatic e-MV coupling with the H_u, T_{1u}, and A_u

TABLE I. Assignments, calculated frequencies ω (cm^{-1}), and half width of the phonon spectrum (cm^{-1}) of H_g and A_g modes of C_{60}^-. The widths of both the adiabatic e-MV origin γ_{ad} and nonadiabatic e-MV origin γ_{nonad} are tabulated. We have assumed $\epsilon_F=0.9$ eV and $N(0)=2.5$ states/eV C_{60}^- per spin for each t_{1u} band.

Mode	$1H_g$	$2H_g$	$1A_g$	$3H_g$	$4H_g$	$5H_g$	$6H_g$	$7H_g$	$2A_g$	$8H_g$
ω	264	452	611	770	926	1262	1408	1585	1661	1709
γ_{nonad}	0.0	0.8	0.5	7.2	3.7	9.9	6.6	11.9	9.4	61.7
γ_{ad}	9.4	16.3	15.1	84.7	25.4	55.9	25.8	70.1	21.1	185.4

[Herzberg-Teller (HT) active] modes brings about interactions with interband mixing between the t_{1u} and the t_{1g} derived bands. The symmetry reduction due to the JT effect[32,33] and a pseudorotation along the Goldstone-like mode makes this group theoretical argument less rigorous. We have included both the t_{1u}-t_{1u} phonon-induced interband mixing and the t_{1u}-t_{1g} phonon-induced interband mixing to calculate nonadiabatic e-MV coupling contribution to the half width of the phonon spectrum of the H_g, A_g, H_u, T_{1u}, and A_u modes. We have used Eq. (16) for the former case and Eq. (18) for the latter case. In adopting these equations, we ignored for simplicity liftings of degeneracies of vibrational modes. We used the parameters $\epsilon_F=0.9$ eV and $N(0)=2.5$ states/eV per spin C_{60}. This corresponds to a total density of state 15 states/eV per C_{60}. The other parameters λ and ω were calculated from the electronic wave function of C_{60}^- obtained with the MNDO approximation.

The calculated half width of the nonadiabatic e-MV coupling origin γ_{nonad} and of the adiabatic e-MV coupling origin γ_{ad} are summarized in Tables I and II. In Table I we found a substantial width of the highest-frequency H_g mode of the nonadiabatic e-MV coupling origin. The other nonadiabatic e-MV coupling origin widths of the H_g, A_g, H_u, T_{1u}, and A_u modes are relatively small. Along with the adiabatic e-MV coupling origin width of the highest-frequency H_g mode, we may be able to observe doping-induced formation of the structure of the highest-frequency H_g mode, which should be assigned to the strong coupling constants of both the adiabatic and the nonadiabatic e-MV couplings in this mode. The highest-frequency H_g modes have very large widths of the adiabatic e-MV coupling origin. We also found large widths of the $3H_g$, $5H_g$, and $7H_g$ modes. (We numbered the vibrational modes in ascending manner with frequencies.) These results are in one of the best agreements with experiments among e-MV theories.[5–7] The agreement suggests that there is no serious breakdown of our lowest-order arguments.

We find in Table II that the symmetry unfavorable $1H_u$, $2T_{1u}$, and $3T_{1u}$ modes have large widths of the adiabatic e-MV coupling origin. The contribution from the nonadiabatic e-MV coupling is very small. The large gap between t_{1u} and t_{1g} derived bands makes it hard to mix these bands via virtual exchange of nuclear momentum. The large contribution from the adiabatic e-MV coupling of some of the ungerade modes indicates that the symmetry reduction by the JT distortion of the order of 0.01 Å changes of C-C bonds puts very dramatic effects on mixing among t_{1u} and t_{1g} derived bands. Experimentally, Kato *et al.* observed the JT distortion of isolated C_{60}^-.[33] It may be difficult to observe the distortion directly in solids, but our results may suggest indirectly the existence of the JT distortion in doped C_{60}. Experimental observation of doping-induced changes of the phonon half width of the ungerade modes is one of the criteria of the JT distortion.

Coupling with T_{1u} modes has been studied by infrared absorption spectroscopy[19,20] and was studied theoretically with the charged-phonon model by Rice and Choi.[22] Recently Prassides *et al.* have observed a broadening of the H_u mode upon doping in the range of 60–70 meV in addition to a T_{1u} mode in that energy region.[21]

The $1H_u$ mode has the largest width of the phonon spectrum among all HT active modes of C_{60}^-. The $2T_{1u}$ and $3T_{u1}$ modes also have substantial width. These results are in qualitative agreement with the experimental results obtained by Prassides *et al.* for the lower-frequency $1H_u$ and $2T_{1u}$ modes.[21] Our results also suggest the coupling with the higher-frequency $3T_{1u}$ mode, which does not contradict another inelastic neutron scattering experimental result by White *et al.*[34]

These agreements may indicate the validity of our e-MV theory and are indicative of the JT distortion in doped C_{60}^-. The e-MV couplings of the H_u and T_{1u} modes can contribute to the electron-phonon mechanism of superconductivity along with the e-MV couplings with H_g modes.

TABLE II. Assignments, calculated frequencies ω (cm^{-1}), and half width of the phonon spectrum (cm^{-1}) of H_u, T_{1u}, and A_u modes C_{60}^-. The widths of both adiabatic e-MV origin γ_{ad} and nonadiabatic e-MV origin γ_{nonad} are tabulated. We have assumed $\epsilon_F=0.9$ eV and $N(0)=2.5$ states/eV C_{60}^- per spin for each t_{1u} band.

Mode	$1H_u$	$2H_u$	$1T_{1u}$	$2T_{1u}$	$3H_u$	H_u	A_u	$5H_u$	$3T_{1u}$	$6H_u$	$4T_{1u}$	$7H_u$
ω	406	564	575	700	706	818	970	1331	1351	1470	1561	1679
γ_{nonad}	1.3	2.9	5.0	3.5	1.8	1.7	3.2	12.2	3.5	3.3	18.5	13.4
γ_{ad}	150.9	29.6	7.2	91.8	17.6	3.6	25.5	2.6	82.9	0.3	10.9	0.1

V. SUMMARY

We have calculated the Lorenzian half widths of intramolecular vibrations of doped C_{60}, which are brought about by adiabatic and the nonadiabatic e-MV coupling. We have succeeded in explaining qualitatively most of the experimental observations related to phonon broadenings with use of the JT mechanism. We have obtained direct theoretical evidence of the non-negligible contributions of the H_u and T_{1u} modes in addition to the H_g modes. We also obtained a substantial width of the phonon spectrum of the nonadiabatic e-MV coupling origin with the highest-frequency H_g mode. The theoretical result agrees with the inelastic neutron scattering results qualitatively. This indicates the vital role of the JT mechanism (including the nonadiabatic e-MV coupling) of superconductivity in doped C_{60}.

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