Excitonic polaron in the photoemission spectra of C_{60}^- and the origin of high-T_c superconductivity of doped fullerenes

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The photoemission spectrum of C_{60}^- is well-described over a wide energy region by the small polaron theory with polaron–exciton coupling. The strongest coupling is found for the A_{g2} pinch mode and an ~0.5 eV Frenkel exciton. © *1995 American Institute of Physics.*

High-temperature superconductivity of doped fullerenes is a challenging problem for the theory. M_xC_{60} seems to be prepared by nature to be (bi)polaronic because of its *bare* nonadiabaticity. The phonon frequencies are high, $\omega \simeq 0.2$ eV, and the bare Fermi energy is very low, $E_F \simeq 0.1$–0.2 eV. The Tolmachev logarithm in the definition of the Coulomb pseudopotential μ^* does not apply in this nonadiabatic case, and the electron–phonon coupling must be strong ($\lambda > 1$) in order to overcome the Coulomb repulsion. A strong electron–phonon interaction implies small polarons. The cluster structure of C_{60} favors bipolarons. Therefore doped fullerene M_xC_{60} is an ideal system in which to observe high-T_c polaronic or bipolaronic superconductivity.[1] However, the final answer to the question on the nature of the superconductivity in these compounds depends not only on the adiabatic ratio ω/D and the coupling constant but also on the characteristic frequency of phonons coupled to the carriers. If a relatively weak coupling ($\lambda \leqslant 0.5$) with low-frequency phonons dominates, the Migdal–Eliashberg theory can be applied with the BCS ground state. On the other hand, if the coupling is strong and (or) high-frequency phonons are involved, the nonadiabatic polaron theory[1] is more appropriate. There are some experimental results, e.g., an ascending temperature dependence of the upper critical field and a short coherence length, which favor the bipolaronic scenario for M_xC_{60},[2] while some others (e.g., the results of tunneling experiments) can be interpreted in terms of the canonical strong-coupling BCS theory.

The recent photoemission spectroscopy (PES) of the C_{60}^- molecule (Ref. 3) allows us to estimate the relative contribution of different phonon modes and other bosonic excitations to the interaction. The variational analysis by Gunnarsson *et al.*[3] showed the strongest coupling with a *low*-frequency H_g mode.

In this letter we analyze the PES data[3] using the exact polaronic diagonalization with respect to the $A_g(2)$ mode and introducing a *polaron–exciton* coupling. We obtain a fit to

the experimental PES data which is just as good as the variational approach[3] for low binding energies and much better for the high-energy region. We obtain the strongest coupling with the high-lying $A_g(2)$ pinch mode and with a Frenkel-type exciton. As a result we provide strong evidence for nonadiabatic strong coupling with high-energy bosonic excitations in M_xC_{60}.

The appropriate Hamiltonian, describing three degenerate t_{1u} states coupled with phonons, is diagonalized with respect to the A_{g2} coupling using the canonical Lang–Firsov displacement transformation

$$S=g\sum_{m=1}^{3}\psi_m^{\dagger}\psi_m(b^{\dagger}-b). \tag{1}$$

The result is

$$\tilde{H}=e^{S}He^{-S}=-E_P^{A_{g2}}\sum_{m=1}^{3}\psi_m^{\dagger}\psi_m+\sum_{\nu=1}^{8}g^{\nu}\omega_{\nu}\sum_{n,m=1}^{3}\psi_n^{\dagger}M_{nm}^{\nu}\psi_m+\sum_{\nu}^{8}\sum_{\mu=1}^{5}\omega_{\nu}n_{\nu,\mu}, \tag{2}$$

where $E_p^{A_{g2}}=g^2\omega_{A_{g2}}$ is the polaron shift due to the A_{g2} mode with the phonon operators b, $b^{\dagger}$, the 3×3 dimensionless matrix $\tilde{M}$ is taken from Ref. 4,

$$\hat{M}=\begin{pmatrix}\sqrt{3}Q_4+Q_5 & \sqrt{3}Q_1 & \sqrt{3}Q_2\\ \sqrt{3}Q_1 & -\sqrt{3}Q_4+Q_5 & \sqrt{3}Q_3\\ \sqrt{3}Q_2 & \sqrt{3}Q_3 & -2Q_5\end{pmatrix},$$

and $n_{\nu,\mu}$ are the phonon occupation numbers of eight fivefold degenerate H_g modes with the phonon operators $Q_{\mu}^{\nu}=b_{\nu,\mu}^{\dagger}+b_{\nu,\mu}$. The interaction with H_g modes is responsible for the dynamic Jahn–Teller effect in C_{60}. According to calculations,[5] singly ionized C_{60}^{-} is in the intermediate coupling regime, while the doubly and triple ionized molecules are in the strong-coupling limit with respect to the coupling with H_g modes. Therefore a reasonable estimate of the ground state energy is obtained by taking into account only the diagonal part of $\hat{M}$. Nevertheless, to avoid any ambiguity we calculated the spectral function $I_{\rm pol}(\omega)$ of the Hamiltonian, Eq. (2) by the exact numerical diagonalization in a truncated Hilbert space (up to 4 phonons) for the H_g modes as described in Ref. 6.[1)] A self-trapped exciton in neutral C_{60} is observed in the luminescence.[7] Because of the polaron–exciton coupling we add the same spectral function to the total spectral density shifted by the exciton energy $\omega_{\rm ex}$ and multiplied by the polaron–exciton coupling constant α:

$$I(\omega)=I_{\rm pol}(\omega)+\alpha I_{\rm pol}(\omega+\omega_{\rm ex}). \tag{3}$$

This is an exact procedure if the interaction with excitons, as with phonons, is linear. Then we integrate $I(\omega)$ with the Gaussian instrumental resolution function of width $\sim$41 meV (Ref. 3), taking into account the damping $\gamma_{\rm ex}$ of the exciton in the second (excitonic) contribution. We thus can fit the PES in a wide energy region as shown in Fig. 1, with g^{ν} being the fitting parameters (inset). The polaron–exciton coupling constant is found to be $\alpha=0.5$, the exciton energy $\omega_{\rm ex}\simeq 0.5$ eV, in agreement with the luminescence data,[7] and the inverse exciton lifetime is estimated to be $\gamma_{\rm ex}\simeq 580\ {\rm cm}^{-1}$. The coupling to the $A_g(2)$ mode turns out most important, in agreement with the tight-binding calculations.[8] If the

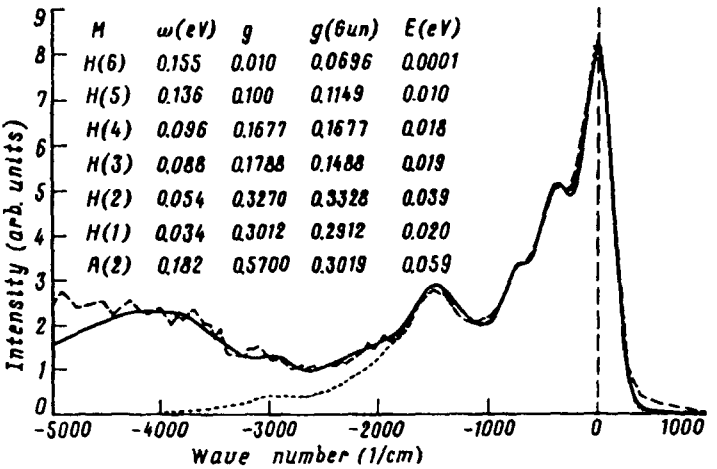

FIG. 1. Polaron theory fit (full line) to the experimental PES (dashed line). The frequencies $\omega=\omega_\nu$, coupling constants $g=g^\nu$, and the contribution to the ground state energy $E=E_p^\nu$ for different modes are shown in the inset. For comparison we also show the coupling constants [g(Gun), inset] and the calculated variational PES (dotted line) from Ref. 3.

phonon frequency is above the polaronic half-bandwidth, the decay of the phonon in electron–hole pairs is prohibited, no matter how strong the electron–phonon coupling is.[9] This fact explains a small value of the $A_g(2)$ linewidth. Contrary to Gunnarsson *et al.*,[3] we found that the coupling with the high-frequency $H_g(7)$ and $H_g(8)$ modes is negligible and that their broadening is so large that in the metallic samples they cannot even be seen. However, we do not believe that their broadening is due to the interaction with the carriers, because Na_xC_{60}, which does not exhibit a metallic state with doping, shows the same strong line broadening of the $H_g(7)$ and $H_g(8)$ modes.[10]

We conclude that the frequencies of the essential bosonic excitations (phonons and excitons) that are strongly coupled with electrons are higher than or of the same order as the electron half-bandwidth in doped fullerenes. This fact, as well as the observation of the phonon and exciton side bands in the PES, in itself favors the nonadiabatic small polaron theory[1] rather than the adiabatic Migdal–Eliashberg approach to M_xC_{60}. We attribute the broad feature located in the fundamental gap region of C_{60}^- to a polaron dressed by a Frenkel-type exciton.

We have profited from valuable and stimulating discussions with J. Ranninger.

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