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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}^{-} in a wide energy region is well described with the small polaron theory and the polaron-exciton coupling. The strongest coupling is found with the pinch A_{g2} mode and with ~ 0.5 eV Frenkel exciton.

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 frequences are high, $\omega \simeq 0.2$ eV and the bare Fermi energy is very low $E_F \simeq 0.1 - 0.2$ eV. Tolmachev *logarithm* in the definition of the Coulomb pseudopotential μ^* does not apply in this nonadiabatic case and the electron-phonon coupling should be strong ($\lambda > 1$) to overcome the Coulomb repulsion. The 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 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 ($\lambda \leq 0.5$) 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 experiments as an upward temperature dependence of the upper critical field and a short coherence length favoring bipolaronic scenario for M_xC_{60} [2] while some others (as example, the tunneling experiments) can be interpreted in terms of the canonical strong-coupling BCS theory.

The recent photoemission spectroscopy of a molecule C_{60}^{-} [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.* showed the strongest coupling with a *low*-frequency H_g mode.

In this letter we analyse the PES data [3] using the exact polaronic diagonalization with respect to the $A_g(2)$ mode and introducing the *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 a strong evidence for the nonadiabatic strong coupling with high-energy bosonic excitations in M_xC_{60}.

The Hamiltonian at hand, describing three degenerate t_{1u} states coupled with phonons, is diagonalised 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

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

where $E_p^{A_{g2}} = g^2 \omega_{A_{g2}}$ is the polaron shift due to the A_{g2} mode with the phonon operators $b, b^\dagger$, 3×3 dimensionless matrix $\hat{M}$ 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 five-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 ionised C_{60}^- is in the intermediate coupling regime, while the doubly and triple ionised 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 diagonal part of $\hat{M}$. Nevertheless, to avoid any ambiguity we calculated the spectral function $I_{pol}(\omega)$ of the Hamiltonian, Eq.(2) by the exact numerical diagonalisation in 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 luminescent [7]. Because of the polaron-exciton coupling we add the same spectral function to the total spectral density shifted by the exciton energy ω_{ex}, and multiplied by the polaron-exciton coupling constant α as

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

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

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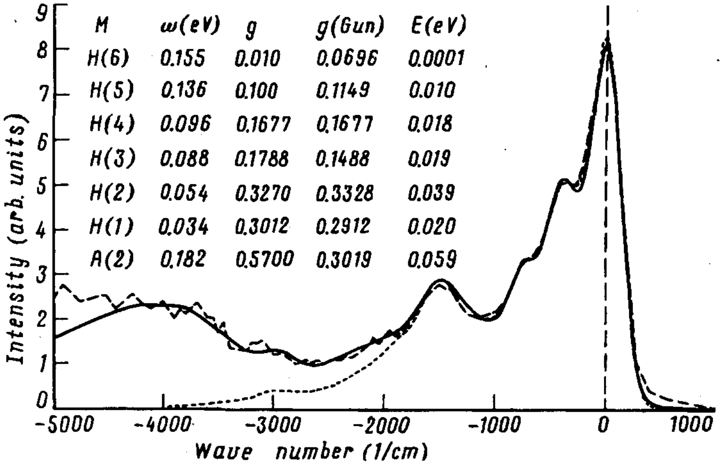
1) The value of the exciton energy $\simeq 0.5\,\mathrm{eV}$ in the gas phase of C_{60}^- is readily obtained using the luminenescence line at $\sim 1.55\,\mathrm{eV}$ and the dielectric constant (~ 5) of the solid C_{60} (see in W.E. Pickett, Solid State Physics, Eds. H. Ehrenreich and F. Spaepen, Academic Press, **48**, 225 (1994)).

coupling is [9]. This fact explains a small value of the $A_g(2)$ line-width. 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 while 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].



M	ω(eV)	g	g(Gun)	E(eV)
H(6)	0.155	0.010	0.0696	0.0001
H(5)	0.136	0.100	0.1149	0.010
H(4)	0.096	0.1677	0.1677	0.018
H(3)	0.088	0.1788	0.1488	0.019
H(2)	0.054	0.3270	0.3328	0.039
H(1)	0.034	0.3012	0.2912	0.020
A(2)	0.182	0.5700	0.3019	0.059

Polaron theory fit (full line) to the experimental PES (dashed line). 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) of ref.[3]

We conclude that the frequences of essential bosonic excitations (phonons and excitons) strongly coupled with electrons are above 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-sided bands in PES by itself favor 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 the polaron dressed by a Frenkel-type exciton.

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