Electron-spectroscopy study of LiC_{60}: Charge transfer and dimer formation

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Li-C_{60} compounds $Li_{\bar{x}}C_{60}$ were studied for average Li concentration $\bar{x}\leqslant 1$ using photoelectron spectroscopy. Strong evidence is found for the formation of LiC_{60} dimers, as well as a second phase. The study suggests that the smallest alkali-metal Li bonds to C_{60} largely ionically for certain configurations. An investigation of the Li 1*s* level shows that under certain conditions the energetics favor a backdonation of the transferred electron to the Li ion.

It is now well established that alkali metals and C_{60} can be combined in a range of concentrations to form various phases with interesting properties. For example, A_3C_{60}, where *A* is K, Rb, or Cs, is an ionically bonded superconductor, whereas A_4C_{60} and A_6C_{60} are insulating phases, the former due to strong electron-electron correlations, and AC_{60} are polymers in the ground state. The case of AC_{60} is somewhat complex, in that a metastable dimer phase and high-temperature-stable rocksalt phase can also be obtained, as well as the fact that the transport properties of these phases vary somewhat depending on the size of the alkali-metal atom.[1] The significantly smaller Li and Na are interesting for their deviations compared to the heavier alkali metals, e.g., the ability to form compounds A_xC_{60} with $x>6$ ($Na_{10}C_{60}$, $Li_{12}C_{60}$),[2–4] and the lack of an ordered $x=3$ phase when intercalating solid C_{60}.[5]

Focusing on the superconducting phases, it has been established that a charge of close to $-3e$ per fulleride is required to obtain superconductivity.[6–8] Na induces a polymer structure in Na_2RbC_{60} and the superconducting critical temperature (T_c) is reduced for this compound. T_c is also low for Na_2KC_{60} compared to a general scheme obeyed by A_3C_{60} compounds containing only heavier alkali metals, in which T_c varies with lattice constant in a simple manner.[9,7] Superconductivity has not been detected in Li-containing Li_2RbC_{60} and Li_2CsC_{60}.[10] It has recently been shown that higher concentrations of Li in the latter material (Li_3CsC_{60}, Li_4CsC_{60}) lead to measurable superconductivity.[7] This is ascribed to a nontotal charge transfer from Li to fullerene, so that a charge donation of $-3e$ per C_{60} is still required for superconductivity to be supported.[7] Na, on the other hand, does donate very close to one electron per alkali-metal atom for concentrations $x\leqslant 6$.[3] The completely exceptional behavior for Li surmised from the observations above has been attributed to Li $2s-C\ 2p$ hybridization.[11]

The previous discussion suggests that C_{60} salts containing Li [as already shown for Na (Ref. 5)] may be expected to exhibit novel structures/properties for $x\leqslant 6$, in addition to those discovered at high concentrations.[2–4] To investigate this idea, we have studied the interaction of Li and solid C_{60} for low dopant concentrations using photoelectron spectroscopy (PES), and find for LiC_{60} strong evidence that a dimer phase and a second phase are formed at room temperature. Simple estimates of the relevant energetics show that complete charge transfer from Li to C_{60} is allowed at very low Li concentrations, as it is for the heavier alkali metals. The level of covalent interaction is more difficult to ascertain for the ground state, as in, e.g., the case of K_4C_{60},[12] but Li 1*s* spectra suggest a strong Li $2s-C\ 2p$ overlap. Our results can be taken as a confirmation that the level of charge transfer to C_{60} is determined by a subtle balance of screening, Madelung, and covalent bonding energies for the smallest alkali-metal Li.

The experiments were carried out at Beamline 22 at MAX-Lab.[13] A thick C_{60} film was evaporated onto a Cu(111) surface for each measurement, with the film thickness determined by the requirement that the spectra did not contain any contribution from the substrate. Li was evaporated onto such films from a well-outgassed SAES getter source. Evaporation times varied from 25 to 120 s, and annealing a representative sample at 100 C for 3 min was found not to change the LUMO-derived portion of the spectra. The O 1*s* region was checked to exclude contamination of the sample. The base pressure in the sample preparation chamber was $<2\times10^{-10}$ Torr, and in the measurement chamber $<7\times10^{-11}$ Torr. Valence PES was recorded at a photon energy of 80 eV with a total resolution of $\sim$0.1 eV. The spectra are given on an absolute binding energy [ionization potential (IP)] scale, determined with reference to the spectrum low-energy cutoff in the standard manner, with special precautions due to the nominally insulating character of the C_{60} films.[14] The IP of pristine solid C_{60} agreed within 20 meV with the previously reported value.[14]

In Fig. 1 two valence spectra of samples containing different amounts of Li in the low Li concentration region are displayed. The lower spectrum is at the lowest Li concentration studied. The ratio of the Li-induced peak area to the HOMO (at an IP of 7.1 eV) is consistent with an average concentration $\bar{x}$ in the vicinity of 1 and lower.[15] It is clear that for $Li_{\bar{x}\leqslant 1}C_{60}$ two peaks appear in the fundamental gap,

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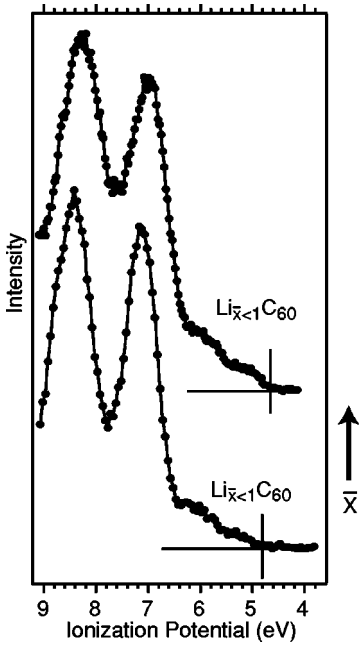

FIG. 1. Valence spectra for the indicated samples; the Li concentration increases towards the top of the figure. The spectra for $\bar{x}<1$ represent mixtures of phases, as described in the text. The spectrometer E_F is indicated by a vertical mark for each spectrum.

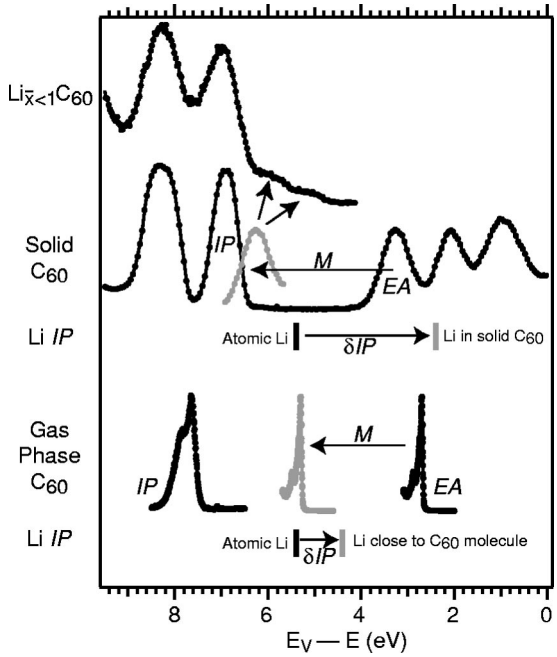

FIG. 2. Density-of-states (DOS) and IP's for the indicated C_{60} and Li systems. The curves for pristine solid C_{60} comprise PE spectra for the occupied and inverse PE spectra for the unoccupied part of the DOS taken from Ref. 22 and calibrated as in Refs. 14 and 23. The gas phase results have also been published previously. (Refs. 24 and 25). δIP is the polarization-induced reduction of the IP. The light gray curves show the Madelung-stabilized LUMO's for gas and solid phase C_{60}, and the light gray marks the polarization modified Li IP's. See the text for more details.

located at about 0.4 and 1.2 eV below E_F of the PES spectrometer. Also clear is that the HOMO and other bands broaden as a result of Li intercalation. We are able to crudely model the spectra as composed of subspectra from three phases—two separate LiC_{60} phases (see discussion below) and pristine C_{60}. For this reason we have chosen to distinguish between average composition ($\bar{x}$) and formula composition (x), the latter being the default.

The double structure for $\bar{x}\approx 1$ has been observed for all other alkali-metal fullerides at room temperature.[16–19] For RbC_{60}, Poirier *et al.*[16] were able to isolate the two features using temperature protocols modeled after x-ray-diffraction results,[20] and showed that they correspond to different phases, namely the metastable dimer phase (higher binding energy) and stable orthorhombic phase (lower binding energy). Two-phase assignments were also made for PES spectra of Na, K, and Cs fullerides, where it was found that samples prepared by evaporation at room temperature show two characteristic LUMO-derived structures for $\bar{x}\approx 1$, with the high-binding-energy (insulating) component assigned to dimeric[18] or polymeric[19] AC_{60}. The assignment of the low-binding-energy component has also varied,[17–19] but there is significant evidence that it is *not* due to a polymer phase—the oxygen sensitivity for KC_{60} is strong, as opposed to the dimeric phase,[19] and the reversible temperature variation of the relative population of the two phases for[18] CsC_{60} suggests that the low-temperature peak might be due to a phase with a rocksalt structure.[19] The dimeric structure was observed in the first study[15] of $Li_{\bar{x}}C_{60}$, whereas the low-binding-energy component was not, which could be due to oxygen contamination as suggested[21] for the Na data in the same study. The characteristic dimer-induced PES structure observed here and common to all other alkali metals strongly suggests that Li bonds very similarly to any larger alkali metal for $x=1$, at least in the surface region of the sample to which PES is sensitive.

To better assess this issue, we evaluate the energetics of charge transfer for LiC_{60} in terms of a Born-Haber cycle.[26] Starting with the LiC_{60} complex in the gas phase, charge transfer entails first the cost of ionization of atomic Li [5.4 eV (Ref. 27)], at which we place the ''unscreened'' Li 2*s* level shown in Fig. 2. However, this cost is reduced by polarization of C_{60} by the resulting Li ion, which is estimated[28] to be $\delta IP_{Li}\approx 1$ eV. Upon transferring the electron to C_{60}, one expects stabilization corresponding to the C_{60} electron affinity (EA) of[24,23] 2.8 eV, plus the Coulomb (''Madelung'') energy, *M*, of isolated LiC_{60} of about 2.6 eV, which in a one-electron picture shifts the now partially occupied LUMO as shown in Fig. 2. Thus the overall energy balance gives $\Delta E = IP - \delta IP - EA - M \approx -1$ eV. From those numbers it is clear that polarization plays a crucial role in the stabilization of the charge-transfer complex.

The picture is not changed qualitatively when considering Li-intercalated solid C_{60}. In the first approximation of a single Li ion inside a C_{60} crystal, we estimate as follows: the Li atom is placed in a tetrahedral site within the fcc lattice, which has been shown to be the preferred site for Na at low concentrations.[5] The distance to the four nearest C_{60} molecules is thus $\sqrt{3}/4$ times the lattice constant [14.17 Å (Ref. 29)]. δIP is then 0.9 eV per C_{60} molecule, i.e., 3.6 eV total. A more realistic calculation should give a somewhat higher contribution,[30] if our assumptions about the geometry are adequate. The EA of solid C_{60} is 3.5 eV (Refs. 14 and 23)

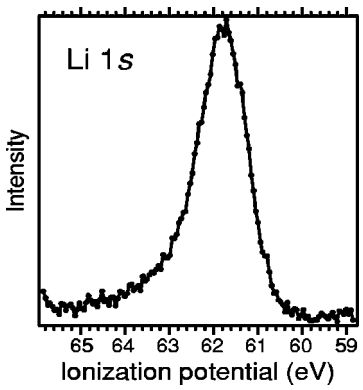

FIG. 3. Li 1*s* spectrum corresponding to the lower spectrum in Fig. 2. The binding energy is close to the one found (Ref. 37) for the 1*s* level in atomic Li minus a polarization-screening term, as described in the text.

and the Madelung energy 2.3 eV for this site.[31] Thus the equation corresponding to total charge transfer is $\Delta E = \mathrm{IP} - \delta\mathrm{IP} - \mathrm{EA} - M \approx -4$ eV. For higher concentrations one would expect a decreased contribution due to polarization on the one hand, with an increase of the Madelung contribution on the other. The cohesive energy of Li of about[32] 1.6 eV/atom is small enough to permit Li bonding to C_{60} according to this scenario as well, at least for low concentrations. Thus total charge transfer would appear to be permitted from energetic considerations for the LiC_{60} complex to a similar extent as for other alkali metals,[33] in both the gas and solid phases.

Figure 2 also shows that our rough estimate of the LUMO IP for the monomer complex lies in the energy range observed for $Li_{\bar{x}\leqslant 1}C_{60}$. An increase of this IP due to dimerization is to be expected due to the opening of a gap,[16,34] but extraction of this parameter from our data is not motivated at present. On the other hand, the insulating character of this phase is a strong indication of a filled band, suggesting a dominatingly C 2*p* character for the states involved.

This picture is further supported by PES data for the NaC_{60}^{-} complex.[35] Na and Li have similar ionic diameters and IP's, so that the case of NaC_{60}^{-} should bear directly on our results. The close agreement between the cases of free C_{60}^{-}, NaC_{60}^{-}, and KC_{60}^{-} is readily apparent.[26,35,24] A Born-Haber cycle analysis along the lines of Fig. 2, and including the extra electron for the negative ions, is quite consistent with total charge transfer for molecular KC_{60},[26] and the shift in EA from KC_{60} to NaC_{60} is consistent with the change in ionic radius from K to Na, which should increase the EA slightly via the Madelung term. Additionally, quantum chemical calculations of the structure of Li-C_{60} complexes indicate C_{60} LUMO character for the orbital containing the least-bound electron in the LiC_{60} molecular complex, as well as others with higher Li content.[36]

Examination of the Li 1*s* level further clarifies the energetics (Fig. 3). The binding energy is about 9 eV too low to correspond to a polarization-screened doubly ionized Li atom in a C_{60} matrix. Much better agreement is achieved if one assumes the Li atom to be singly ionized as shown by the following analysis: The binding energy of the 1*s* electron in atomic Li is about 64.5 eV for the Li^{+} triplet final state ^3S.[37] Polarization reduces this value by $\delta\mathrm{IP} = 3.6$ eV for the tetrahedral and $\delta\mathrm{IP} = 3$ eV for the octrahedral sites to yield $E_{\mathrm{B}}^{\mathrm{Li}\ 1s} = 60.9$ eV and 61.5 eV, respectively. This is in relatively good agreement with the experimental value of 61.8 eV and suggests a backtransfer of an electron into the Li 2*s* level upon 1*s* ionization. The fast transfer process implied by the photoemission measurement points at a large overlap between the Li 2*s* and the C_{60} LUMO-derived orbitals in the ground state. This confirms the observation from transport measurements that Li exhibits unique charge-transfer characteristics, with a greater propensity toward forming covalent bonds, and suggests that even for LiC_{60} the system is not far from the borderline between the charge-transfer and covalent bonding regimes.

Thus, we have shown that $Li_{\bar{x}}C_{60}$ compounds for $\bar{x} \approx 1$ are characterized by largely ionic bonding as for all other alkali metals. In particular, a dimer phase for LiC_{60} has been identified. An investigation of the Li 1*s* level has shown that a fast electron transfer back onto the Li ion can take place under suitable circumstances. This behavior lends support to the interpretation of the finding that there is a disparity between Li and Na in their effect on superconductivity for, e.g., Li_2CsC_{60} and Na_2CsC_{60}, and the fact that Li appears able to donate less than one electron per alkali-metal atom in such compounds.[7] Those results would therefore appear to be due to specifics of the location of the smaller alkali-metal atoms, a suggestion also motivated by recent theoretical work.[12] It could be worthwhile to revisit the problem of the Li_xC_{60} phase diagram at low concentrations in detail.

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