Electron-spectroscopy study of LiC60: Charge transfer and dimer formation

Schnadt, Joachim; Brühwiler, Paul A.; Mårtensson, Nils; Lassesson, Andreas; Rohmund, Frank; Campbell, Eleanor E. B.

Published in:
Physical Review B (Condensed Matter)

2000

Document Version:
Publisher's PDF, also known as Version of record

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Electron-spectroscopy study of LiC$_{60}$: Charge transfer and dimer formation

J. Schnadt, P. A. Brühwiler, and N. Mårtensson
Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden

A. Lassesson, F. Rohmund, and E. E. B. Campbell
School of Physics and Engineering Physics, Gothenburg University and Chalmers Institute of Technology, SE-412 96 Gothenburg, Sweden

(Received 28 October 1999; revised manuscript received 9 March 2000)

Li-C$_{60}$ compounds Li$_x$C$_{60}$ were studied for average Li concentration $\bar{x} \approx 1$ 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 ionicly for certain configurations. An investigation of the Li 1s 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$_x$C$_{60}$, where A is K, Rb, or Cs, is an ionically bonded superconductor, whereas A$_x$C$_{60}$ and A$_x$C$_{60}$ are insulating phases, the former due to strong electron-electron correlations, and A$_x$C$_{60}$ are polymers in the ground state. The case of A$_x$C$_{60}$ is somewhat complex, in that a metastable dimer phase and hightemperature-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. 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$_x$C$_{60}$ with $x > 6$ (Na$_{10}$C$_{60}$, Li$_{12}$C$_{60}$)$_{2-4}$ and the lack of an ordered ground state, as in, e.g., the case of K$_4$C$_{60}$. Superconductivity has not been detected in Li-containing alkali-metal Li. 

Focusing on the superconducting phases, it has been established that a charge of close to $-3e$ per fulleride is required to obtain superconductivity. Na induces a polymer structure in Na$_2$RbC$_{60}$ and the superconducting critical temperature ($T_c$) is reduced for this compound. $T_c$ is also low for Na$_2$KC$_{60}$ compared to a general scheme obeyed by A$_x$C$_{60}$ compounds containing only heavier alkali metals, in which $T_c$ varies with lattice constant in a simple manner. Superconductivity has not been detected in Li-containing Li$_2$RbC$_{60}$ and Li$_2$CsC$_{60}$. It has recently been shown that higher concentrations of Li in the latter material (Li$_3$CsC$_{60}$, Li$_4$CsC$_{60}$) lead to measurable superconductivity. 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. Na, on the other hand, does donate very close to one electron per alkali-metal atom for concentrations $x \approx 6$. The completely exceptional behavior for Li surmised from the observations above has been attributed to Li 2s–C 2p hybridization.

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 $x \approx 6$, in addition to those discovered at high concentrations. 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$_4$C$_{60}$. but Li 1s 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. 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 1s region was checked to exclude contamination of the sample. The base pressure in the sample preparation chamber was $< 2 \times 10^{-10}$ Torr, and in the measurement chamber $< 7 \times 10^{-11}$ 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. The IP of pristine solid C$_{60}$ agreed within 20 meV with the previously reported value.

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. It is clear that for Li$_{\bar{x} < 1}$C$_{60}$ two peaks appear in the fundamental gap,
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 fullerenes at room temperature. For RbC$_{60}$, Poirier et al. were able to isolate the two features using temperature protocols modeled after x-ray-diffraction results, 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 fullerenes, 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 or polymeric AC$_{60}$. The assignment of the low-binding-energy component has also varied, 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, and the reversible temperature variation of the relative population of the two phases for CsC$_{60}$ suggests that the low-temperature peak might be due to a phase with a rocksalt structure. The dimeric structure was observed in the first study of Li$_2$C$_{60}$, whereas the low-binding-energy component was not, which could be due to oxygen contamination as suggested 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. 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 2s level shown in Fig. 2. However, this cost is reduced by polarization of C$_{60}$ by the resulting Li ion, which is estimated to be $\delta IP_L \approx 1$ eV. Upon transferring the electron to C$_{60}$, one expects stabilization corresponding to the C$_{60}$ electron affinity (EA) of 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. The distance to the four nearest C$_{60}$ molecules is thus $\sqrt{3}/4$ times the lattice constant [14.17 Å (Ref. 29)]. $\delta IP$ 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, 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.\textsuperscript{31} Thus the equation corresponding to total charge transfer is $\Delta E = \text{IP} - \delta\text{IP} - \text{EA} - \langle\text{M}\rangle = -4$ 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\textsuperscript{12} 1.6 eV/atom is small enough to permit Li bonding to C\textsubscript{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\textsubscript{60} complex to a similar extent as for other alkali metals,\textsuperscript{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$_x$C\textsubscript{60}. An increase of this IP due to dimerization is to be expected due to the opening of a gap,\textsuperscript{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 dominantly C $2\,p$ character for the states involved.

This picture is further supported by PES data for the NaC\textsubscript{60} complex.\textsuperscript{35} Na and Li have similar ionic diameters and IP’s, so that the case of NaC\textsubscript{60} should bear directly on our results. The close agreement between the cases of free C\textsubscript{60}$^-$, NaC\textsubscript{60}$^-$, and KC\textsubscript{60}$^-$ is readily apparent.\textsuperscript{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\textsubscript{60}.\textsuperscript{26} and the shift in EA from KC\textsubscript{60} to NaC\textsubscript{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\textsubscript{60} complexes indicate C\textsubscript{60} LUMO character for the orbital containing the least-bound electron in the LiC\textsubscript{60} molecular complex, as well as others with higher Li content.\textsuperscript{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\textsubscript{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 $^3S$.\textsuperscript{37} Polarization reduces this value by $\delta\text{IP} = 3.6$ eV for the tetrahedral and $\delta\text{IP} = 3$ eV for the octahedral sites to yield $E_b^{\text{Li}^+} = 60.9$ 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\textsubscript{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\textsubscript{60} the system is not far from the borderline between the charge-transfer and covalent bonding regimes.

Thus, we have shown that Li$_x$C\textsubscript{60} compounds for $x = 1$ are characterized by largely ionic bonding as for all other alkali metals. In particular, a dimer phase for LiC\textsubscript{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$_2$CsC\textsubscript{60} and Na$_2$CsC\textsubscript{60}, and the fact that Li appears able to donate less than one electron per alkali-metal atom in such compounds.\textsuperscript{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.\textsuperscript{12} It could be worthwhile to revisit the problem of the Li$_x$C\textsubscript{60} phase diagram at low concentrations in detail.

We acknowledge stimulating discussions with K. Prassides, L. Forro, G. Oszlanyi, and E. Tosatti, kind permission by the authors of Ref. 24 to use their data, and financial support from Naturvetenskapliga forskningsrådet (NFR) and the Consortium on Clusters and Ultrafine Particles, which is financed by Stiftelsen för Strategisk Forskning.


A. Gutiérrez and S.L. Molodtsov, J. Phys.: Condens. Matter 9, 11 151 (1997), these authors have no direct measure of the structure, and the large band gap consistent with the high-binding-energy structure is much more easily reconciled with a dimer, rather than polymer, structure.


Polarization of the C_{60} molecule was estimated from the molecular polarizability α of C_{60} and assuming point dipoles. α=1130 Å^3×ε_0 from the permittivity ε (4.4 [see, e.g., G. Gensterblum et al., Phys. Rev. Lett. 67, 2171 (1991)]) using the Clausius-Mossotti relation. We assume that Li binds to C_{60} at a distance that is the sum of the Li ionic radius (0.8 Å) and one-half the C_{60} ball outer diameter of (Ref. 38) 10.3 Å.


The total energy gain decreases to 3 eV for occupation of an octahedral site. Also, the Madelung energy will be reduced slightly to the extent that polarization of C_{60} reduces the effective Li charge.


As an estimate, we take K, for which the IP is about 1 eV less than Li, giving a stabilization of ~4 eV, similar to the value given in Ref. 12.


