

# LETTERS TO THE EDITOR

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## COMMUNICATIONS

### Electronic structure of $K_xC_{60}^-$ in the gas phase

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The recent discovery of electrical conductivity<sup>1</sup> and superconductivity<sup>2</sup> in alkali-doped buckminsterfullerene has stimulated great interest in understanding the basic physical and chemical properties of these materials.  $C_{60}$  has many unique chemical and physical properties which can be attributed to its unusually high symmetry and stability.<sup>3</sup> In fact, the electric conductivity of the  $A_xC_{60}$  materials ( $A = K, Rb, Cs$ ) can be understood on the basis of the molecular electronic structure of  $C_{60}$ , which has a triply degenerate lowest unoccupied molecular orbital (LUMO) with a highest occupied molecular orbital (HOMO)-LUMO gap of 1.7 eV (Ref. 4) and can accept up to six electrons. In the  $A_xC_{60}$  materials, the alkali atom donates its outer  $s$  electron to the triply degenerate LUMO of  $C_{60}$ , forming a partially filled conduction band and a largely ionic compound. Photoemission experiments<sup>5</sup> have shown the appearance of a characteristic metallic Fermi edge as the alkali atom is doped into the  $C_{60}$  lattice. The insulating property of the  $A_6C_{60}$  compounds indicates that not only is there charge transfer in the  $A_xC_{60}$  compounds, but also the highly ionic  $C_{60}^{6-}$  configuration is stable in solid compounds.<sup>6</sup> What is surprising is the unusually high transition temperature of superconductivity found in these materials.<sup>7</sup> Infrared and Raman scattering experiments<sup>8</sup> have revealed important information about intramolecular vibrations of  $C_{60}$  in the  $A_xC_{60}$  compounds, which should be of great importance to elucidate the superconducting mechanism in these materials. Also of relevance to the superconductivity are the intermolecular vibrations, which have hereunto not been observed.

To understand the fundamental molecular interactions and electronic structures in the  $A_xC_{60}$  molecules, where the alkali atom is outside the  $C_{60}$  cage, we have initiated an investigation of the  $A_xC_{60}$  molecules in the gas phase. In this letter, we report two sets of experiments on  $K_xC_{60}^-$ . The first is the photoelectron spectroscopy (PES) of  $K_xC_{60}^-$ , which reveals the electronic energy levels of the isolated  $K_xC_{60}$  molecules and valuable information about the nature of the K- $C_{60}$  interaction. Secondly, by scanning a dye laser over the detachment threshold of  $KC_{60}^-$  we have detected a series of vibrational autodetachment resonances,

providing the first measure of the frequency of the K- $C_{60}$  stretching vibration.

The details of the experimental setup have been described before.<sup>9,10</sup> To generate internally cold  $K_xC_{60}^-$  species, we used a large "waiting room" nozzle version of a dual-valve pulsed supersonic cluster beam source with laser vaporization.<sup>10</sup> The target was a 1 cm diam  $K_6C_{60}$  pellet, prepared following literature procedure<sup>11</sup> using about 250 mg raw toluene-extracted  $C_{60}$  sample. Typically, 2 mJ output from a Q-Switched Nd:YAG laser was focused to 1 mm diam on the target, vaporizing the target material into the gas phase, followed by a supersonic expansion through a 1.5 mm diam nozzle with He carrier gas. After being skimmed by a 6 mm diam skimmer, the negative ions in the beam were extracted perpendicularly at 1 KV into a time-of-flight mass spectrometer (TOFMS). The negative ions were separated by mass in time and space in the TOFMS and were intercepted downstream by various detaching lasers in a magnetic time-of-flight electron spectrometer. The predominate negative ions were found to be  $C_{60}^-$  and  $KC_{60}^-$ . In addition,  $K_2C_{60}^-$  and  $K_3C_{60}^-$  were also observed, but with successively reduced signal strengths. A small amount of  $C_{70}^-$  and  $KC_{70}^-$  were also present because the original fullerene sample was not chromatographically purified. Two types of lasers were employed for the PES study: an ArF excimer laser (6.42 eV) provided a wider energy range while the third harmonic (3.51 eV) of a Nd:YAG laser yielded more accurate measurements of detachment thresholds. Moreover, there was no background photoelectron signal at 3.51 eV photon energy, enabling PES spectra of the weak-signal  $K_2C_{60}^-$  and  $K_3C_{60}^-$  species to be obtained. Electron TOF spectra were taken for each species and then converted into energy, using  $Au^-$  as calibration. The study of vibrational autodetachment resonances was performed by monitoring near-threshold electron signals while tuning a dye laser in the energy range of the  $KC_{60}^-$  detachment threshold.

Figure 1 shows the PES spectrum of  $KC_{60}^-$  along with that of  $C_{60}^-$  at 6.42 eV photon energy. Except for an energy shift the  $KC_{60}^-$  spectrum is nearly identical to that of  $C_{60}^-$ , indicating the energy levels of  $C_{60}$  are intact in

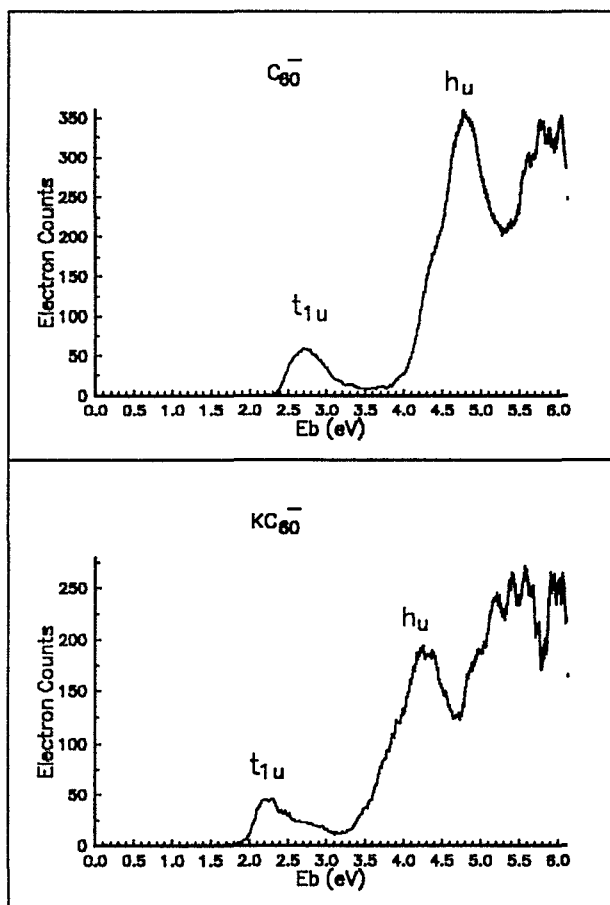


FIG. 1. Photoelectron spectra of  $C_{60}^-$  and  $KC_{60}^-$  at 6.42 eV photon energy. Eb stands for the electron binding energy.

$KC_{60}^-$ . This suggests that there is a charge transfer from K to  $C_{60}$  so that the  $C_{60}$   $t_{1u}$  LUMO is filled with two electrons and the  $K^+$  ion acts as a spectator. This is supported by the apparent increase of the  $t_{1u}/h_u$  PES intensity ratio from  $C_{60}^-$  to  $KC_{60}^-$ . We can estimate the electron affinity (EA) of  $KC_{60}$  by assuming a  $K^+$  ion interacting with a  $C_{60}^{2-}$  ion. We assume that  $EA(KC_{60})$  equals  $EA(C_{60}^-)$  plus a Coulomb attraction (CA) of the outgoing electron by  $K^+$ . CA is approximated to be 1.8 eV by using the ionic radius of  $K^+$  and assuming a 5 Å van der Waals radius for  $C_{60}^{2-}$ . We take  $EA(C_{60}^-)$  to be  $EA(C_{60})$  minus an electron-electron repulsive energy for two point charges on a 3.5 Å radius sphere (the radius of  $C_{60}$ ), which is roughly 2.1 eV. Using the recently measured EA of  $C_{60}$  (2.65 eV),<sup>10</sup> we get  $EA(C_{60}^-)$  to be 0.45 eV, which is in good agreement with a recent pseudopotential calculation.<sup>12</sup> Thus our estimated EA of  $KC_{60}$  is 2.25 eV, which is in excellent agreement with our measured value (Fig. 2). Hence, the K- $C_{60}$  bond is highly ionic and  $KC_{60}^-$  can be approximately described as  $K^+C_{60}^{2-}$  in the gas phase.

It is interesting to draw an analogy between alkali halide molecules and  $KC_{60}$ , where  $C_{60}$  acts like a strong electronegative halogen atom. In fact,  $C_{60}$  maintains its size and nearly spherical shape in many chemical and physical

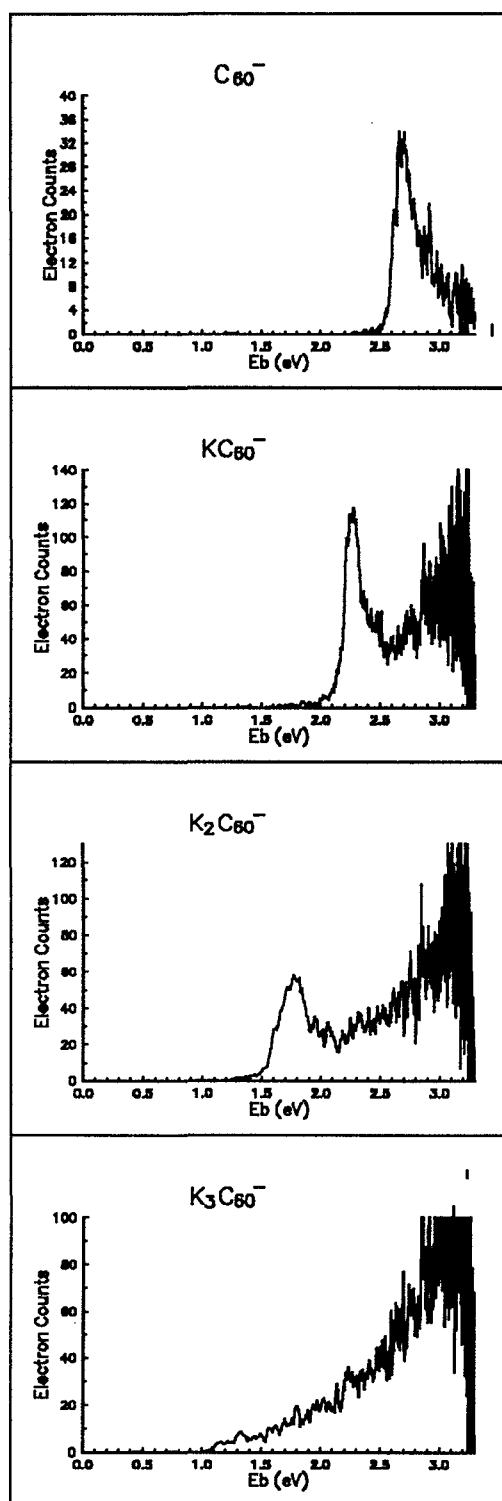


FIG. 2. Photoelectron spectra of  $K_xC_{60}^-$  ( $x=0-3$ ) at 3.51 eV photon energy.

environments, exhibiting a single atomlike entity. This atomlike behavior of  $C_{60}$  has recently been emphasized in a proposal<sup>13</sup> which even gives it an "elemental" symbol (Bf). However, there is a major difference between  $KC_{60}^-$  and the alkali halide negative ions. The extra electron in the

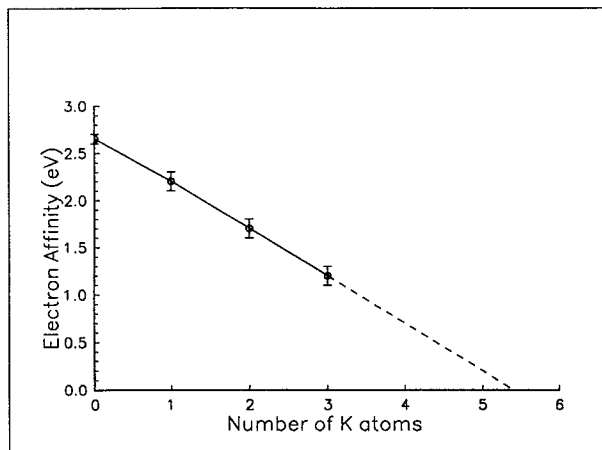


FIG. 3. Electron affinity of  $K_xC_{60}$  vs the number of K atoms.

alkali halides is localized on the alkali atoms<sup>14</sup> while it is on  $C_{60}$  in  $KC_{60}^-$  due to its extremely high multielectrophilicity.

Figure 2 displays the PES spectra of the  $K_xC_{60}^-$  species ( $x=0-3$ ) at 3.51 eV photon energy. The EA ( $2.2 \pm 0.1$  eV for  $KC_{60}$ ,  $1.7 \pm 0.1$  eV for  $K_2C_{60}$ , and  $1.2 \pm 0.1$  eV for  $K_3C_{60}$ ) decreases as the number of K atom increases, and the K-containing species all have substantial low energy electron signals, similar to that seen previously<sup>10</sup> in hot  $C_{60}^-$  due to electron-“phonon” scatterings, i.e., the outgoing electrons lose energy to molecular vibrations. The  $K_xC_{60}^-$  species have more low frequency vibrations related to the K atoms in addition to the already numerous intra- $C_{60}$  vibrations. Thus, one expects to see increasingly more low energy signals in  $K_xC_{60}^-$  due to these electron-phonon scatterings. The effect of thermionic emission observed previously<sup>10</sup> from hot  $C_{60}^-$  ions should also be enhanced in  $K_xC_{60}^-$  due to their lower EAs and should contribute as well to the low energy signals.

Figure 3 is a plot of the dependence of the EAs as a function of the number of K atoms. The EAs were determined from the peak maxima, based on the spectrum of  $C_{60}^-$  for which an accurate EA was measured previously.<sup>10</sup> A clear linear relationship is exhibited. Based on a purely electrostatic model, the EAs of the  $K_xC_{60}$  species are determined by the differences of the  $K^+ - C_{60}^{n-}$  Coulomb attraction, the electron-electron repulsion in  $C_{60}^{n-}$ , and the polarization interactions between  $K_x^+ C_{60}^{x-}$  and  $K_x^+ C_{60}^{(x+1)-}$ . It can be shown that these differences are linearly dependent on  $x$ , indicating that the higher  $K_xC_{60}^-$  species are also quite ionic. This is understandable since, in comparison to the condensed phase, the Coulomb attraction can be optimized (no lattice constraint) and there are no  $C_{60}^{n-} - C_{60}^{n-}$  repulsions in the gas phase. So the electronic energy levels of  $K_xC_{60}^-$  and their PES spectra should be very similar to that of  $C_{60}^-$ , except for  $x=3$  and 4 where there should be a spin-spin splitting for removing an electron from the  $t_{1u}$  LUMO, which is now more than half-filled, causing a splitting of the first peak in their PES spectra. The lack of a sharp peak in the  $K_3C_{60}^-$  spectrum

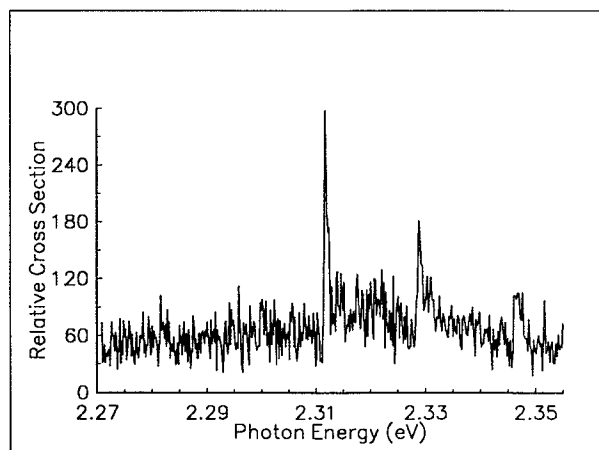


FIG. 4. Near threshold spectrum of  $KC_{60}^-$  (546–526 nm, 0.08 nm resolution) showing three vibrational autodetachment resonances.

seems to be in agreement with this argument, because the splitting could not have been resolved and merely results in a broadening of the spectrum. A more definitive answer will have to wait for a higher resolution study and for PES spectra of the larger  $K_xC_{60}^-$  at a higher photon energy. A detailed quantum calculation would also be very useful.

A more challenging problem is to study the vibrational spectroscopy of  $K_xC_{60}^-$ . In particular, information about the intermolecular vibrations would be highly valuable. Autodetachment through a dipole-supported state has been shown to be a prominent technique to study the spectroscopy of negative ions.<sup>15</sup> A dipole-bound state, in which an electron is bound in a diffuse orbital by a molecular dipole field, is analogous to a Rydberg state in neutral molecules. It was predicted<sup>16</sup> that there exist an infinite number of such states above a critical dipole moment (1.625 D) for a fixed dipole. Garrett<sup>17</sup> subsequently showed that the critical dipole moment is dependent on the dipole length, moment of inertia, and molecular rotations, and that there are, in general, only a limited number of dipole-bound states. They have recently been observed in a few negative ions.<sup>15,18</sup> Such states are very weakly bound relative to electron detachment and yield in the total detachment cross section sharp resonance features through rotational or vibrational autodetachments. With high resolution lasers, very detailed spectroscopic information has been obtained for these negative ions. Being highly ionic, the  $KC_{60}$  molecule should have a large dipole moment and may support such dipole-bound states.

Figure 4 shows a spectrum of  $KC_{60}^-$ , obtained by monitoring near threshold electrons while continuously scanning a dye laser (from 546 nm to 526 nm) at a resolution of 0.08 nm around the detachment threshold. We observe a series of three equally spaced peaks, which can be readily assigned as vibrational autodetachment resonances through a dipole-bound state, as discussed above. The spacings are  $140 \text{ cm}^{-1}$ , which must be due to an inter-K- $C_{60}$  vibration since the lowest intra- $C_{60}$  vibration is  $273 \text{ cm}^{-1}$ . Most likely, this is the K- $C_{60}$  stretching vibration because the K- $C_{60}$  interaction has abruptly

changed from  $K^+ - C_{60}^{2-}$  in the ground state of  $K^+ - C_{60}^-$  in the upper dipole-bound state. The first peak at 2.3116 eV is above the detachment threshold. If it is the origin, then this state is only quasibound. If this state is truly bound, the origin could not have been accessed through the one-photon autodetachment, rather it can only be observed through a two-photon process. We tried to look for such two-photon signals, but did not observe any. Thus, it is possible that the state is a quasibound, dipole-supported state. Assuming the first peak is the origin, a simple Franck-Condon factors calculation yielded a bond distance change of about 0.08 Å. The lack of any apparent hot band features indicates that the  $K C_{60}^-$  molecule was rather vibrationally cold, better than  $\sim 150$  K as estimated from the Franck-Condon factor calculations. The first peak at 2.3116 eV has a width of  $3 \text{ cm}^{-1}$ , giving a 2 ps lower limit to its lifetime. A higher resolution scan at  $0.3 \text{ cm}^{-1}$ , limited by the laser, did not reveal any fine structure.

Dipole-bound states have not been observed in the analogous alkali halides negative ions although they were thought to be ideal systems for studying dipole-bound states.<sup>18(d)</sup> The explanation given was that such states are too tightly bound due to their strong dipoles. This gives rise to too long-lived excited vibrational-rotational levels of the dipole-bound states for them to be observable on the given experimental time scale.<sup>18(d)</sup> In comparison, the unusually large size of the  $C_{60}^-$  ion in  $K C_{60}$  perhaps makes the outer electron feel more repulsion, leading to a more weakly dipole-bound or even quasibound states which could more rapidly autodetach.

In conclusion, we have studied the photoelectron spectroscopy of  $K_x C_{60}^-$  in the gas phase. The electron affinities of these species are found to depend on the number of K atoms linearly. This leads to the conclusion that these species are quite ionic, in that, the K atom each donates its outer 4s electron to the  $t_{1u}$  LUMO of  $C_{60}$ , similar to that found in the bulk alkali-doped  $C_{60}$  materials and demonstrating the unique multielectron-affinity character of the  $C_{60}$  molecule. A dipole-supported state was found in  $K C_{60}^-$ , yielding an inter-K- $C_{60}$  stretching vibration of  $140 \text{ cm}^{-1}$ .

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