Intra- and extramolecular vibrations of fulleride surfaces

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The surfaces of K-doped C_{60} thin films have been studied by high-resolution electron energy loss spectroscopy in reflection geometry. In addition to showing the expected intramolecular infrared-active modes of T_{1u} symmetry, as well as their usual behavior upon doping, the K_4C_{60} and K_6C_{60} phases display two K-related, dipole-active, extramolecular phonons. In K_3C_{60}, the electronic screening limits the dipolar probing depth to the topmost layer and only one K-related phonon is observed. Our data also reveal that the Raman-active A_g vibrations dominate the intramolecular energy region. The properties and the modified K/C_{60} stoichiometry of the outmost surfaces of fullerides are discussed accordingly.

I. INTRODUCTION

Since C_{60} (Ref. 1) has been available in sizable quantities,[2] its vibrational excitations have often been investigated, especially because phonons are expected to play an important role in the high-temperature superconducting phase,[3] but also because they probe the molecular environment and provide an alternative way to enlighten our understanding of fullerene surfaces and interfaces. Here we are concerned with the surface properties of intercalation-doped C_{60}, such as K_3C_{60}, which presents a moderate transition temperature of 18 K.[4] In recent years, it has been proposed that the extreme surface of doped fullerenes, like K_3C_{60}, may possess specific properties compared to the bulk of the compound. This concept has been discussed in the light of photoemission experiments[5] and electron energy loss spectroscopy (EELS) studies.[6] Here, we report on a high-resolution EELS (HREELS) study of K_3C_{60}, K_4C_{60}, and K_6C_{60} thin crystalline films and discuss the properties and stoichiometry of their respective surfaces.

While isolated, C_{60} belongs to the I_h point group, so that only the four T_{1u} modes are infrared (IR) active and the two A_g and eight H_g modes are Raman active. In the solid state, the intramolecular phonons can be regarded as "on-ball" excitations slightly perturbed by the molecular environment.[7] However, solid-state condensation induces the appearance of extramolecular excitations (below 200 cm^{-1}) associated with the rotational and translational degrees of freedom of the isolated molecules. Librations and translational bulk excitations have been measured by far-infrared and Raman spectroscopies,[8] as well as inelastic neutron scattering (INS).[9–11] Inelastic He scattering revealed surface librations and Rayleigh waves.[12,13] The intercalation of alkali atoms in C_{60} gives rise to additional vibrational excitations, in addition to modifying the intramolecular phonons because of the charge transfers. Raman,[14] high-resolution EELS (HREELS),[15] INS, and theoretical investigations have focused on those excitations in K- and Rb-doped C_{60} films.[16–19] In short, the observed frequencies probe the alkali atom site and the nature of the doping atoms, as well as their stoichiometry with respect to C_{60}. The HREELS technique allows the observation of both extra- and intramolecular vi-

brations and is sensitive to their dipolar character. In addition, the limited probing depth of the technique restricts the analysis to the surface, enabling the investigation of its properties. The high resolution achieved here allows us to separate the excitations of the topmost C_{60} layer from those of the layers underneath, providing a deeper understanding of the surface properties of fullerides.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Fullerene thin films (about ten C_{60} layers) were obtained by sublimating C_{60} (99.9% purity, MER Corporation) from a resistively heated Ta crucible, on a clean Cu(111) [or Ag(111)] single crystal kept at room temperature. In order to improve the quality of the films, one pure C_{60} monolayer was always predeposited at 600 K (550 K), and a low deposition rate was used (about 15 min per C_{60} layer). After completion of the fullerene film growth, doping was achieved by evaporating potassium from a commercial source (SAES Getter). Adequate K dosing, monitored by Auger electron spectroscopy (AES), and subsequent annealing at about 570 K (550 K) allowed us to obtain thin films of single phases of K_xC_{60} ($x=0$, 3, 4, and 6). The distillation procedure used here may induce fullerene evaporation and therefore hampers a precise determination of the final film thickness. Hence, only estimations (though supported by AES and HREELS) can be given. The base pressure in the ultrahigh-vacuum preparation chamber was about 3×10^{-10} Torr.

HREELS was performed with a Delta 0.5 spectrometer (Vacuum Science Instruments) capable of a resolution of 8 cm^{-1} (evaluated from the full width at half maximum of the elastic peak). In this study, the routine resolution was about 15 cm^{-1}. The electron beam incidence and analysis angles (given in the figure captions) are measured with respect to the surface normal. The primary energy was set at 4 eV. All spectroscopic investigations were carried out at room temperature in a vacuum of about 7×10^{-11} Torr. In addition to AES, the purity and composition of the different phases were checked by recording electronic excitation spectra with the HREELS spectrometer. Those data (not shown here) were
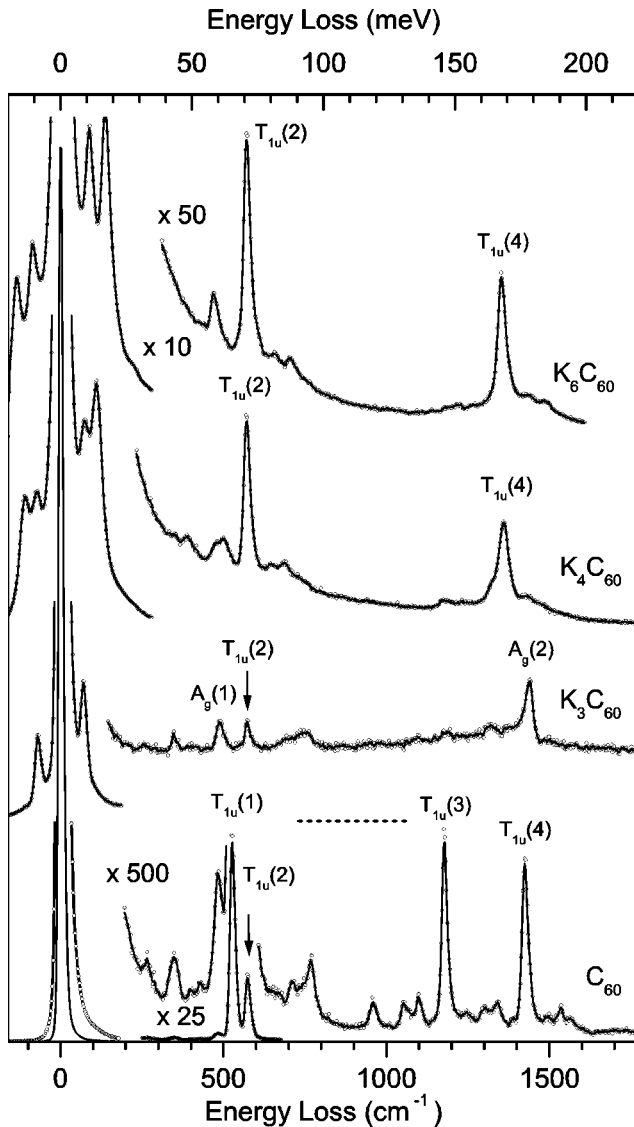
FIG. 1. Vibrational excitation spectra of C_{60}, K_3C_{60}, K_4C_{60}, and K_6C_{60} thin films (from bottom to top), recorded in specular geometry. The incidence angles are respectively 75°, 55°, 65°, and 65°. For all spectra, the primary energy is 4 eV and the resolution is about 15 cm^{-1}. The spectra are normalized with respect to the elastic peak intensity, and the scale factors of the blown-up sections are indicated on the figure.

FIG. 2. Intramolecular vibrations of C_{60} and K_3C_{60} films presented in the energy ranges of the $A_g(1)$ (left panel) and $A_g(2)$ (right panel) modes. From bottom to top, the curves correspond to off-specular data of C_{60} and to off-specular and specular data of K_3C_{60}. Note that the relatively intense background observed in Fig. 1 for K_3C_{60} is not reproduced here for clarity.

measured with a primary energy of 10 eV and a low resolution of about 20 meV. Good agreement with literature data[20] was found for all phases.

III. RESULTS AND DISCUSSION

A. Intramolecular vibrations

The specular spectrum of pure C_{60} shown[36] in Fig. 1 (lower trace) agrees well with previously published HREELS data of multilayers grown on Ag(111) (Ref. 21) or Si(100)-H(2×1) (Ref. 22). The four dominant modes are located at 527, 574, 1177, and 1424 cm^{-1} and all exhibit a clear dipolar character, as their intensities are drastically reduced in off-specular geometry. Obviously, they correspond to the four intramolecular T_{1u} infrared-active modes of C_{60}.[23]
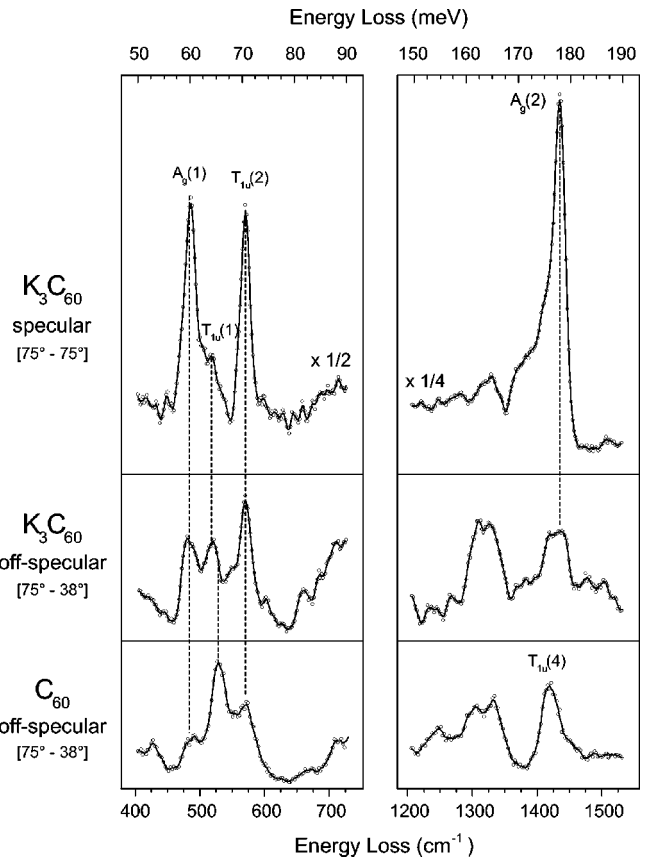
Many peaks appear in the corresponding off-specular spectrum[37] (parts of this spectrum are shown in the lower trace of Fig. 2). Their frequencies match those measured in specular geometry, and some of them show a small dipolar contribution, which could stem from the loss of the icosahedral symmetry of C_{60} in the bulk or at the surface of the film.

The vibrational excitation spectra of K_3C_{60}, K_4C_{60}, and K_6C_{60} thin films, recorded in specular geometry, are also displayed in Fig. 1. For all C_{60} phases, we measured the off-specular spectra as well. In our interpretation, we assume that the dipolar and impact interactions dominate the vibrational fingerprints measured in the specular and off-specular directions, respectively.

In the K_4C_{60} and K_6C_{60} specular spectra of Fig. 1, the peaks visible in the intramolecular frequency range are easily interpreted, owing to the large set of infrared data from the literature.[24,25] In both cases, the spectra are obviously dominated by the $T_{1u}(2)$ and $T_{1u}(4)$ modes, which are located at 572 and 1359 cm^{-1} in K_4C_{60} and at 572 and 1352 cm^{-1} in K_6C_{60}, respectively. The increase of their infrared activity with doping[26] is well reproduced here.

Contrary to the spectra of K_4C_{60} and K_6C_{60}, the HREELS spectrum of K_3C_{60} does not match the corresponding infrared data, although it is clearly dipolar. However, this spec-

trum shows remarkable similarities with the energy loss spectrum of one C_{60} monolayer adsorbed on metals like Ag(111) (Ref. 21) or Cu(111) (Ref. 27). Dipolar modes are observed at 348, 486, 571, and 1438 cm^{-1}. As in the case of C_{60} monolayers adsorbed on metal, we propose to assign the peaks at 486 and 1438 cm^{-1} to the $A_g(1)$ and $A_g(2)$ vibrations of C_{60} and the peak at 571 cm^{-1} to the $T_{1u}(2)$ mode.

It is tempting to explain the discrepancy between the infrared-absorption and the dipolar HREELS fingerprints by invoking the different probing depths of the two techniques. From the dielectric theory of HREELS,[28] we estimate a probing depth of about ten molecular layers for C_{60}, as well as for K_4C_{60} and K_6C_{60}. However, if the substrate is metallic, strong screening is expected and the probing depth should be drastically reduced. As K_3C_{60} is known to be metallic at room temperature,[29] we can infer that the dipolar modes detailed here above are localized in the topmost layer of the K_3C_{60} film. The intense and rather constant background (within the energy range presented here) observed on the specular spectrum testifies to the existence of free carriers, as it corresponds to the left wing of the t_{1u} plasmon peak (located at 0.6 eV), characteristic of the metallic state. In addition, the very low intensity of the $T_{1u}(2)$ mode compared to the other phases is an independent proof of the reduced dipolar probing depth in K_3C_{60}.

A_g molecular vibrations are only Raman active in the icosahedral symmetry. Because the inversion symmetry is broken at the bulk surface, these modes can nevertheless gain some infrared activity. Indeed, a deformation of the molecule at the surface may explain the small infrared activity of the $A_g(2)$ observed when C_{60} is physisorbed on hydrogenated Si(111) (Ref. 30) and on CO-dosed Cu(100) (Ref. 31 and 32). However, this argument is unable to justify the intense infrared activity of the A_g modes measured here and at C_{60}/metal interfaces.[21,27,31-33] This phenomenon has been previously explained by the occurrence of a dynamic charge transfer at the C_{60}/metal interface[33] or by couplings involving the $A_g(2)$ mode, a low-frequency mode (the frustrated translation has been suggested), and induced surface states arising from the hybridization between the molecular and substrate electronic states.[31,32] Therefore, we infer that these processes also occur at the topmost layer of K_3C_{60}, as a result of the metallic character of the underlying fulleride film.

Depending on the preparation procedure, oxidation stages of $C_{60}^{2.5-}$ or $C_{60}^{1.5-}$ have been identified for the topmost layer of K_3C_{60} films.[5] The lower valence is found when the sample is obtained via the distillation method. The frequencies of the intramolecular modes are very sensitive to the charge carried by the C_{60} molecules. Consequently, the high surface sensitivity of our HREELS data of K_3C_{60} allows us to discuss the effective oxidation stage of C_{60}. In Fig. 2, we show K_3C_{60} data recorded in specular and off-specular geometry, restricted to the energy ranges of the $A_g(1)$ (left panel) and $A_g(2)$ modes (right panel), respectively. Off-specular data of undoped C_{60} are added for comparison. In the left panel, one can follow the evolution of the $A_g(1)$, $T_{1u}(1)$, and $T_{1u}(2)$ modes. A clear 11 cm^{-1} downshift of
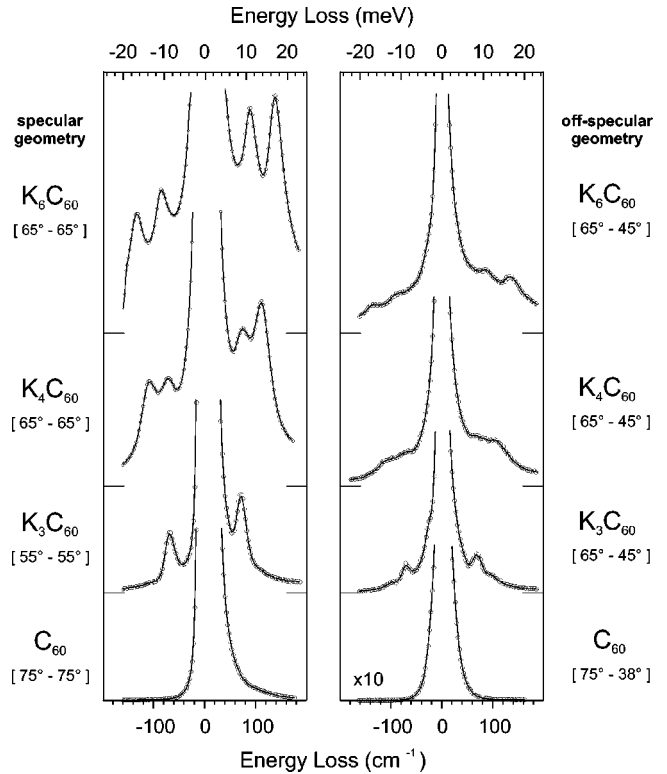

FIG. 3. Energy loss and gain spectra of C_{60}, K_3C_{60}, K_4C_{60}, and K_6C_{60} in the extramolecular vibrational range, recorded in specular (left panel) and off-specular (right panel) geometry.

the $T_{1u}(1)$ mode is observed from C_{60} to K_3C_{60}. Assuming a linear downshift with doping and using bulk infrared data[24] to calibrate the relation of the frequency versus the charge transfer, one obtains about one electron per C_{60} for the K_3C_{60} surface. The $A_g(2)$ mode frequency of 1438 cm^{-1} (right panel) falls between the values of 1432 and 1445 cm^{-1} reported by HREELS for one monolayer of C_{60} adsorbed on Cu(111) (Ref. 27) and Ag(111) (Ref. 21), respectively. The metal substrates donate about 1.5 (Ref. 34) and 0.75 (Ref. 35) electrons per C_{60} for those interfaces, so that a charge transfer of about one electron is acceptable for the K_3C_{60} surface. Consequently, our data confirm that the distillation method produces an underdoped surface.

The infrared intramolecular fingerprint of the K_3C_{60} surface, obtained by HREELS, is thus different from the bulk one, measured by infrared spectroscopy. This difference between the surface and bulk dielectric properties is confirmed, and extended to all fullerides, by the investigation of the extramolecular phonon frequency range, discussed in the next section.

B. Extramolecular vibrations

Intense, low-energy, dipolar losses and gains are well resolved below 200 cm^{-1}, in the HREELS spectra of fullerides (Fig. 1). For the sake of clarity, they are reproduced in the left panel of Fig. 3 and all the frequencies are reported in Table I (along with their off-specular values). One single peak is observed at 71 cm^{-1} for K_3C_{60}; two peaks are

TABLE I. Frequencies (in cm^{-1}) of the extramolecular excitations of fulleride thin films, observed by HREELS in the specular direction and (given in brackets) in off-specular geometry.

	Outmost layer	Internal layers
K_3C_{60}	71 (69)	—
K_4C_{60}	72 (74)	108 (102)
K_6C_{60}	88 (85)	135 (136)

present at 72 and 108 cm^{-1} for K_4C_{60} and at 88 and 135 cm^{-1} for K_6C_{60}. All these peaks are observed both as energy gains and losses. The off-specular counterparts are shown in the right panel of Fig. 1. In the case of K_3C_{60}, an additional shoulder and a peak are detected, respectively, at 27 and 99 cm^{-1} in the off-specular data. By comparison with INS studies[16,17] and theoretical works,[18] the 27 cm^{-1} feature is attributed to librations of the C_{60} molecules. The peak detected at 99 cm^{-1} is ascribed to a combination of the libration and the 71 cm^{-1} peak.

In a previous work, we have shown that K-doped C_{60} monolayers adsorbed on Ag(111) display one characteristic low-frequency dipolar excitation, whose frequency varies as a function of the compound stoichiometry. For K_1C_{60} it is located at 63 cm^{-1} and its frequency increases with K doping.[21] As such excitations are absent from the spectra of undoped C_{60} monolayers and multilayers, these low-frequency modes are related, in both doped monolayers and multilayers, to alkali versus C_{60} displacements rather than to lattice phonons of the C_{60} host crystal.

Regarding K_4C_{60} and K_6C_{60}, it is interesting to determine the nature of the dipolar activity of these modes. Indeed, in these nonmetallic compounds, the probing depth of the dipolar coupling mechanism is about ten fullerene layers, so that both extreme surface and bulk excitations are probed at the same time. Calculations, of the bulk phonon density of states, that include alkali atoms in the C_{60} matrix give either two peaks at 80 and 117 cm^{-1} for Rb_6C_{60} (Ref. 18) or one broad peak at 150 cm^{-1} for K_6C_{60} (Ref. 19). The dipole-active phonon measured at 135 cm^{-1} for K_6C_{60} matches this energy range predicted for the alkali-C_{60} vibrations of bulk, fully doped C_{60}. The modes observed here could thus be of the same nature as the calculated excitations. It is also possible that they actually are Fuchs-Kliewer phonons, which are known to develop at the interfaces of ionic materials. Although we are not aware of similar computations for the K_4C_{60} phase, we attribute the peaks on the K_4C_{60} spectrum to excitations comparable to those of K_6C_{60}.

In order to clarify the origin of those vibrations, we grew K_4C_{60} films of various thicknesses, ranging from about four to ten monolayers. The corresponding spectra are shown in the upper panel of Fig. 4. All spectra were recorded in the same geometry (55°-55°). The highest-frequency peak appears very much affected by the sample thickness and, obviously, grows as the thickness increases. We also performed an angular analysis of the four-layer thick K_4C_{60} sample and report the data in the lower part of Fig. 4. In specular
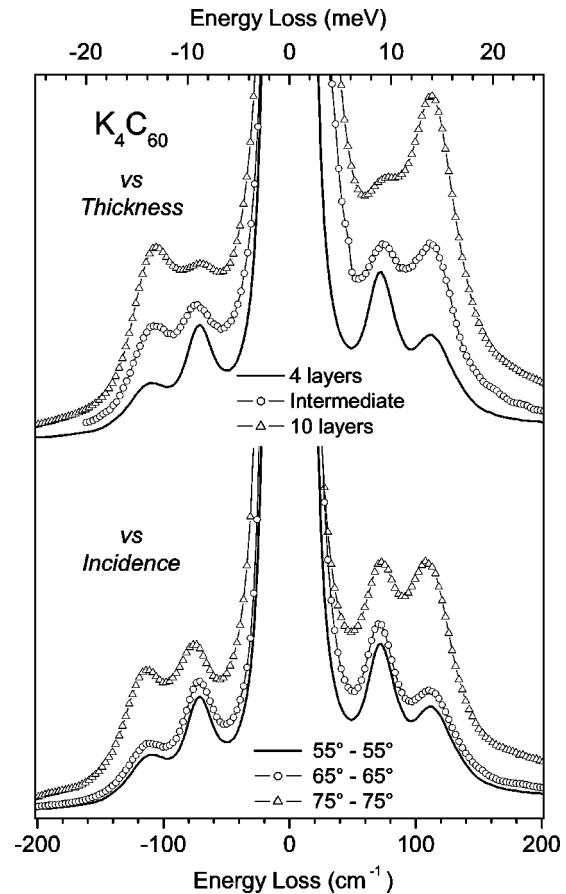

FIG. 4. Evolution of the specular energy loss and gain spectra of K_4C_{60} in the extramolecular vibrational range, with respect to the thickness of the film (top) and to the incidence angle of the electron beam (bottom).

HREELS, the intensity of the two modes increases with the angle of incidence of the electron beam, with a clear enhancement when the angle is rotated towards 75°, which definitively confirms their dipolar activity. However, the effect is again more pronounced for the highest-energy peak. All those measurements can be accounted for by the dielectric theory of HREELS if the peak at 72 cm^{-1} is restricted to the surface and the one at 108 cm^{-1} is allowed to originate from the layers underneath. A similar behavior is observed in the case of K_6C_{60} and the same interpretation is proposed.

In the face-centered-cubic structure of K_3C_{60}, all tetrahedral and octahedral sites are necessarily filled by K atoms. Phonon density of states calculations for the alkali-C_{60} matrix give one peak at 140 (Ref. 19) or 129 cm^{-1} (Ref. 18) for K in the tetrahedral site and another one at 50 (Ref. 19) or 32 cm^{-1} (Ref. 18) for K in the octahedral site. INS effectively shows one peak[17] at 113 cm^{-1}. In the extramolecular energy range, our specular spectrum of K_3C_{60} (Fig. 3) displays only one dipolar peak at 71 cm^{-1}, whose frequency does not match any of the expected values. We argued previously that, in K_3C_{60}, only the top layer excitations can be observed because of the metallic nature of this fulleride. Therefore, we assign the peak to a surface excitation that does not exist in the bulk, by analogy with K_4 and K_6C_{60}.

IV. CONCLUSIONS

Our measurements allow us to sort out (Table I) the extramolecular excitations recorded by HREELS for K_3C_{60}, K_4C_{60}, and K_6C_{60} thin films. The peaks observed at 71, 72, and 88 cm^{-1} originate from the topmost C_{60} layer of the films and the ones at 108 and 135 cm^{-1} come from the layers underneath. The lower frequency of the surface excitations reflects an underdoped stoichiometry in the uppermost C_{60} layer of all fullerides studied here. In the case of K_3C_{60}, the discussion of the intramolecular phonons already led to that conclusion. On doped monolayers, frequencies of 63, 77, and 92 cm^{-1} are found for K_1C_{60}, K_2C_{60}, and K_4C_{60} stoichiometries.[21] Consequently, the observation here of a peak at 71 cm^{-1} plays in favor of a stoichiometry of about 1 or 1.5 K atom per C_{60} for the top layer of K_3C_{60}. A similar stoichiometry can be inferred at the K_4C_{60} surface. The higher frequency of the surface mode in K_6C_{60} can be interpreted as being due to a higher superficial K/C_{60} ratio of about 3.

In the layers inside the fulleride crystals, each C_{60} molecule shares electrons with the surrounding alkali atoms, which are accommodated under and above the fullerene planes. Consequently, the existence of underdoped surfaces can be explained solely by the partial or total removal of the layer of alkali atoms that should rest above the last C_{60} plane and does not require any geometrical reconstruction of the surface. The method used to prepare the films is probably a key factor in the determination of the stoichiometry of the external C_{60} layer. The distillation-based procedure we used is expected to produce the lowest surface doping for all phases as the annealing is likely to remove all upper K atoms. In this case, the surfaces are indeed expected to have a stoichiometry twice lower than their bulk one, in full agreement with our data.

The different probing depths of the HREELS technique for the fulleride films analyzed here reflect the metallic character of the bulk of K_3C_{60} and the semiconducting/insulating nature of the K_4C_{60} and K_6C_{60} films. However, the observation below 90 cm^{-1} of one huge dipole-active extramolecular excitation in the topmost layer of all fullerides suggests a weak screening of the vibrations at their surfaces as well as a reduced stoichiometry of the uppermost layer, questioning again[5,6] the metallic character of the K_3C_{60} surface.

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[36] In the specular spectrum of C_{60}, peaks are observed at 266, 347*, 399, 429, 483*, **527***, **574***, 711*, 767*, 960*, 1054*, 1069, 1098*, **1177***, 1246, 1303, 1341, **1424***, 1494, 1536*, and 1565 cm^{-1}. The frequencies of the dipole-active modes are indicated by a * and the T_{1u} phonon ones are in boldface. The peaks at 1054 and 1098 cm^{-1} are assigned to the energy losses of 2 $T_{1u}(1)$ and 2 $T_{1u}(2)$ phonons, respectively.

[37] On the C_{60} off-specular spectrum, peaks are observed at 263, 347, 404, 427, 490, 527, 570, 668, 711, 765, 829, 959, 1073, 1176, 1252, 1308, 1336, 1423, 1459, 1493, 1519, and 1564 cm^{-1}.