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An in situ spectrochemical study of the reduction of thin fullerene films

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Dedicated to Professor A. Neckel on the occasion of his 75th birthday

Abstract

The reduction of thin fullerene films has been investigated in the presence of different cations in acetonitrile using cyclic voltammetry and in situ attenuated total reflection FTIR spectroscopy. Solution cast and hot wall beam epitaxy films of C_{60} were studied in a three-electrode spectroelectrochemical cell, using a reflection element of germanium covered with platinum as the working electrode. The cyclic voltammetric response is highly dependent on the preparation method of the film and on the electrolyte solution. The infrared spectral changes observed during the reduction processes of C_{60} films show the formation of different reduction states depending on the electrolyte. In the case of Li^+, K^+ and TBA^+ containing electrolytes C_{60}^{2-} is obtained either in one or in two steps. With Na^+ only C_{60}^- is found. In the case of Rb^+, mixed reduction states 1–4 are found. The IR bands during electrochemical reduction in Rb^+ containing electrolyte solution do not indicate the electrochemical formation of the stable RbC_{60} polymeric phase as obtained by vapour doping with Rb. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The discovery of stable fullerenes [1] and in particular the discovery of the preparation techniques for large amounts of fullerenes [2] led to a rapid increase in the number of publications reported on this allotrope of carbon. Fullerenes readily accept up to six electrons [3] resulting in fulleride anions and in particular doped fullerene films produced by evaporation of alkali metals in vacuum have attracted interest due to their special properties such as superconductivity discovered in A_3C_{60} compounds [4] and complex structural and electronic phase transitions observed in A_1C_{60} [5,6].

When C_{60} is doped by vacuum evaporation with the alkali metals K or Rb, stable crystalline phases are formed for A_1C_{60}, A_3C_{60}, A_4C_{60} and A_6C_{60} (A = K, Rb) [7]. Alkali metal doping of C_{60} films has been reported to proceed differently depending on the alkali metal used [8]. The difference in the size of the doping cation influences the structure of the doped C_{60} film. Smaller cations like Na^+ penetrate the C_{60} structure more easily than larger cations like Rb^+. Depending on the amount of steric strain in the film caused by the dopand the solid can either keep the face centered cubic structure of the pristine crystal or transform to a body centered cubic or tetragonal structure [8].

In particular, the discovery of the A_1C_{60} phase increased the research in this field [9]. The A_1C_{60} phase was shown to consist of linear polymer chains [5] at room temperature and to be stable in air when doped with Rb or K [10]. The A_1C_{60} compounds are reported to have a face centered cubic rocksalt structure at high temperatures, which, upon slow cooling, undergoes a

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reversible first order phase transition to an orthorombic state. The C_{60} molecules become chemically bonded and form a polymer by [2 + 2] cycloaddition as proposed in Ref. [11].

Extensive studies on the electrochemistry of fullerene or fulleride films focused on the reduction processes of C_{60} have been reported during recent years [12]. Electrochemistry facilitates the study of the different redox steps in the doping of C_{60} films under controlled conditions. In similar studies of C_{60} solutions in aprotic solvents six consecutive reversible one-electron electroreductions have been detected [3]. The redox chemistry of fullerene films differs considerably from that in fullerene solutions. It is more complicated than the one-electron reduction steps that have been observed in solution. Electroreduction of films allows doping with a high number of different alkali metals as well as organic cations. Electrochemical results reported are from C_{60} film studies made both in aqueous [13] and in organic solvent solutions [12]. Electroreduction, however, is strongly dependent on the structure of the fullerene film deposited. Therefore different results are reported from experiments made under identical conditions but with differently prepared films such as by solution casting, vapor deposition, or by electrochemical deposition. Solution cast films have a non-uniform, porous structure where the size of crystallites can exceed the average thickness of the film. Vapor deposited films on the other hand are usually compact and have a well ordered structure. The experimental work with fulleride films is complicated due to the high solubility of some of the C_{60}^{n-} anions in organic polar solvents [14]. With cyclic voltammetry of C_{60} solid films, usually two reversible redox reactions and a third irreversible reduction are observed [15]. Besides the structure and the solubility of the phases formed upon reduction, the most important factor determining the electrochemical behaviour of the film is the nature of the electrolyte cation. The incorporation of different cations during electrochemical reduction induces the formation of new different phases in C_{60}. Structural changes occurring upon cation incorporation were demonstrated by X-ray diffraction studies [16].

Fourier transform infrared (FTIR) spectroscopy is a powerful tool in obtaining information on structural and molecular properties of fullerenes. The infrared spectrum of C_{60} contains four strong intramolecular modes F_{1u} at $\omega_1 = 526$, $\omega_2 = 576$, $\omega_3 = 1182$ and $\omega_4 = 1428 \text{ cm}^{-1}$ [17]. FTIR studies on alkali metal doping of C_{60} showed that the shift of the IR modes due to doping correlates with the number of electrons transferred to the C_{60} molecule and is barely dependent on the nature of the dopand [17]. In particular, the position of the F_{1u} mode at $\omega_4 = 1428 \text{ cm}^{-1}$ is known to be sensitive to the number of charges on the C_{60} molecule.

By combining independent measuring techniques several parameters can be recorded simultaneously and a more extensive study can be made on the same sample under identical conditions. The combination of FTIR spectroscopy and electrochemistry belongs to the group of techniques that can be made in situ and is referred to one of the techniques counted under spectroelectrochemistry. In the present work, spectroelectrochemical measurements during electroreduction of C_{60} films using cyclic voltammetry and FTIR spectroscopy with the attenuated total reflection (ATR) technique [18–21] are presented. FTIR spectra were recorded in situ during the reduction (electrochemical doping) of C_{60} films in the presence of organic and alkali metal cations. C_{60} films were prepared either by solution casting or by the hot wall beam epitaxy technique and were measured at low temperatures to decrease the solubility of the reduced species. Furthermore, we compared the difference between solid C_{60} films doped electrochemically in the presence of a Rb^+ containing electrolyte and the structure of a C_{60} film when doped with Rb from vapour phase.

2. Experimental

Film preparation of C_{60} was made by solution casting of C_{60} dissolved in dichloromethane or by hot wall beam epitaxy (hwbe) growth with a film thickness of 200–1000 nm [22]. For decreasing the solubility of the reduced C_{60} species, electrochemical doping was made in a temperature controlled spectroelectrochemical three-electrode cell. The measurements were performed at -5 °C. The ATR-FTIR setup has been described in detail elsewhere [18–21]. The cell used is shown in Fig. 1.

A germanium reflection element covered with a thin layer of Pt was used as the working electrode (electrochemical area 0.63 cm²), Ag wire covered with AgCl as the reference (+ 180 mV vs. SHE) and Pt foil as the counter electrode. The spectroelectrochemical experiments were made during potential scanning at a scan rate of 5 mV s⁻¹.
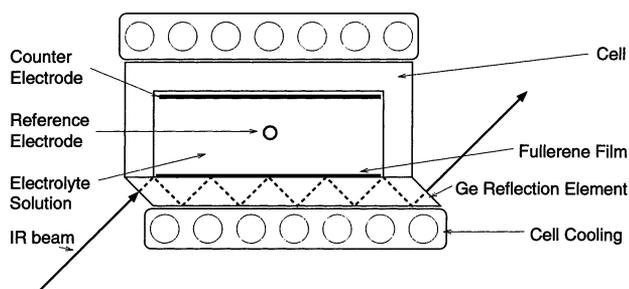

Fig. 1. Three-electrode temperature controlled spectroelectrochemical cell for in situ FTIR–ATR measurements.
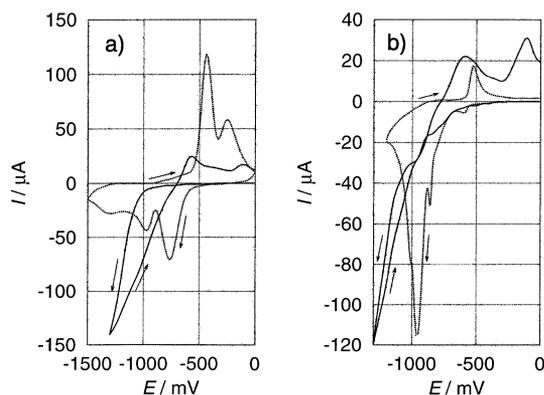
Fig. 2. Cyclic voltammograms of C_{60} films (first cycles). (a) 0.1 M TBAClO$_4$ + acetonitrile electrolyte solution, (b) 0.1 M LiClO$_4$ + acetonitrile electrolyte solution. Solid lines: hwbe films, dotted lines: drop cast films. Scan rate 5 mV s^{-1}.
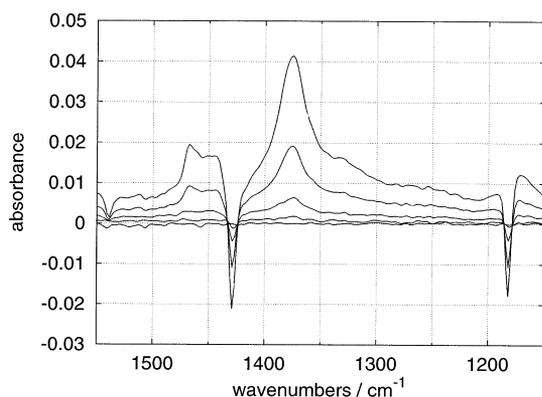

Fig. 3. In situ difference FTIR spectra during reduction of a hwbe C_{60} film in 0.1 M TBABF$_4$ + acetonitrile electrolyte solution. First cycle, reference spectrum around -950 mV, spectra in the range -1000 to -1300 mV.

Acetonitrile (Aldrich) freshly distilled over calcium hydride was used as the solvent. Electrolyte solutions were 0.1 M TBAClO$_4$ (TBA = tetrabutylammonium), TBABF$_4$, LiClO$_4$, KPF$_6$, NaBF$_4$ and 0.01 M RbBPh$_4$ (due to the low solubility of RbBPh$_4$ in acetonitrile). The electrochemistry was controlled by a Jaissle potentiostat and the spectra were recorded by a Bruker IFS66S FTIR spectrometer with an MCT detector. The spectral resolution was 4 cm^{-1}. Spectral changes were recorded consecutively during slow potential scans. For each spectrum 32 interferograms were coadded, which cover a range of approximately 90 mV in the cyclic voltammogram. The spectra measured during reduction of the fullerene film are compared to a spectrum recorded just before the redox reaction. The spectra are related to this reference spectrum and show the spectral changes during the process. Upwards extending peaks are from vibrations of substances created during the process, whereas downwards pointing peaks correspond to material consumed.

3. Results and discussion

3.1. Cyclic voltammetric results

In Fig. 2 the cyclic voltammetric responses of a drop cast and a hwbe deposited C_{60} film during reduction in the presence of TBA$^+$ and Li$^+$ are compared.

The influence of the structure on the electrochemical response can be clearly seen. In the hwbe films (solid lines in Fig. 2), the response from the electrochemical doping reaction is retarded and the two first reductions are not resolved. The reoxidation charge is smaller than the reduction charge, indicating partial dissolution or destruction of the film. With Li$^+$, the reduction of the hwbe film is more structured in the cyclic voltammogram compared to TBA$^+$.

The electrochemical response for solution cast films are shown as dotted lines in Fig. 2. In the presence of TBA$^+$ a quite stable, well-resolved and reversible voltammogram over the two first reduction steps was obtained. With Li$^+$, a large reduction peak with prepeaks, which have been interpreted to originate from partial film dissolution [12], can be seen. Multiple reduction peaks often merging together in a single large cathodic wave is a common feature for the reduction of a C_{60} film in the presence of small cations [12].

As can be seen, the cyclic voltammetric response of the reduction of a C_{60} film is highly dependent not only on the structure and on the morphology of the film, but also on the electrolyte solution. The dependence of the electrochemical response on the structure has been explained by variations in the degree of steric hindrance in the film, by the level of diffusion of electrolyte ions through the film, and by competing chemical reactions (e.g. dimerization, polymerization) occurring parallel to the electrochemical reaction [12].

3.2. In situ FTIR spectroscopy results

Due to the different electrochemical behaviour of C_{60} films in different electrolyte solutions, the respective electrochemical responses do not occur always at the same potential. The spectra shown in this section are measured during the actual reduction process, with the reference spectrum just before the process. The potential regions in different electrolyte solutions may vary.

In situ FTIR difference spectra of a hwbe deposited C_{60} film recorded during electrochemical reduction (first cycle) in the presence of TBA$^+$ are shown in Fig. 3.

A decrease of the band at 1428 cm^{-1} and an increase of the band at 1375 cm^{-1} occur simultaneously upon reduction. The negative bands at 1182 cm^{-1} (F$_{1u}$(3) mode of C_{60}) and 1539 cm^{-1} (either the F$_{2g}$(4) mode of C_{60}, becoming IR active in the solid state, or a combination mode G$_g$(2) ⊗ H$_u$(2) [23]), are correlated with the partial dissolution or destruction of the film, as men-

tioned in section 1 (also seen in Figs. 4–8). During reoxidation (not shown), a two step process is observed by a band appearing at 1393 cm^{-1} during the current
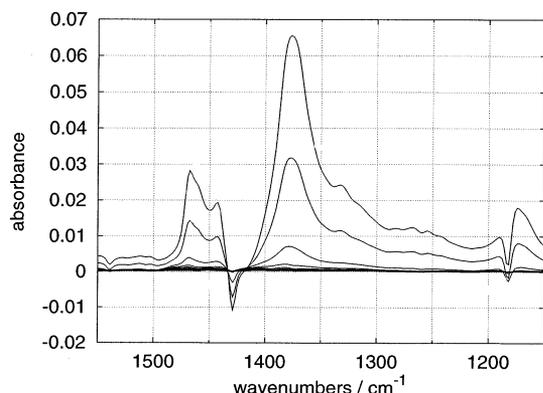

Fig. 4. In situ difference FTIR spectra during reduction of a hwbe C_{60} film in 0.1 M LiClO$_4$ + acetonitrile electrolyte solution. First cycle, reference spectrum around -550 mV, spectra in the range -600 to -1300 mV.
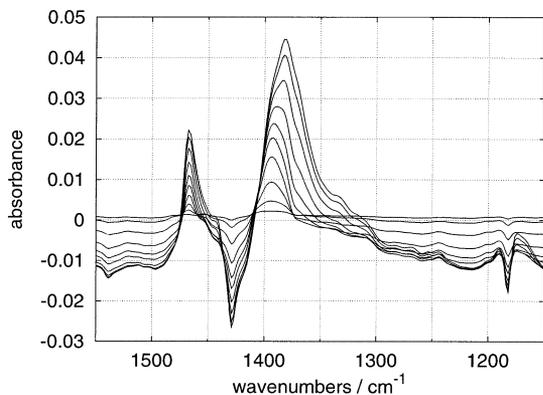

Fig. 5. In situ difference FTIR spectra during reduction of a hwbe C_{60} film in 0.1 M LiClO$_4$ + acetonitrile electrolyte solution. Second cycle, reference spectrum around -550 mV, spectra in the range -600 to -1300 mV.
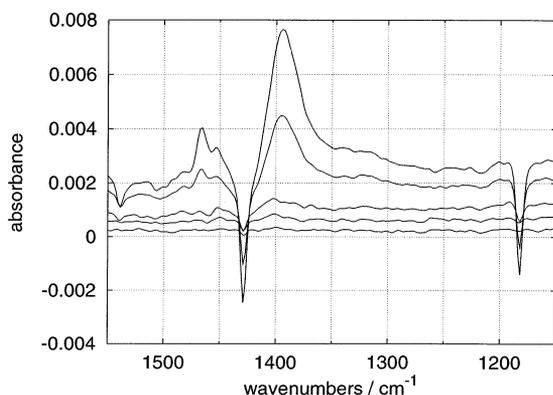

Fig. 6. In situ difference FTIR spectra during reduction of a hwbe C_{60} film in 0.1 M NaBF$_4$ + acetonitrile electrolyte solution. First cycle, reference spectrum around -650 mV, spectra in the range -700 to -900 mV.
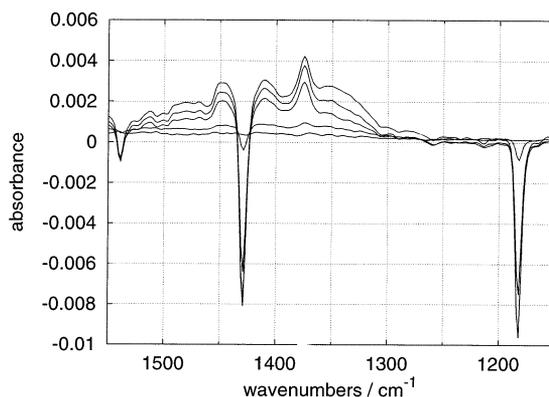

Fig. 7. In situ difference FTIR spectra during reduction of a hwbe C_{60} film in 0.1 M KPF$_6$ + acetonitrile electrolyte solution. First cycle, reference spectrum around -750 mV, spectra in the range -800 to -1200 mV.
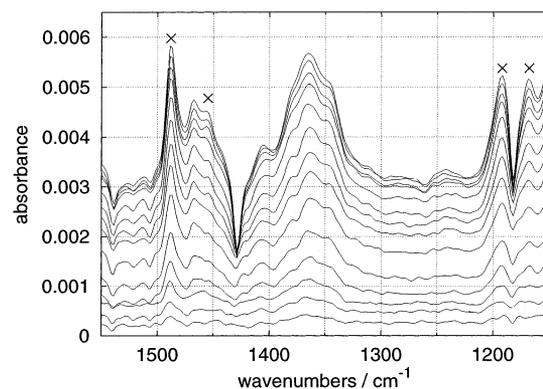

Fig. 8. In situ difference FTIR spectra during reduction of a drop cast C_{60} film in 0.01 M RbBPh$_4$ + acetonitrile electrolyte solution. First cycle, reference spectrum around -400 mV, spectra in the range -450 to -1200 mV. Bands from the electrolyte solution are marked with $\times$ in the figure.

peak around -600 mV and a second band at 1428 cm^{-1} during further reoxidation to 0 mV [24–26]. According to the literature, bands around 1390 and 1375 cm^{-1} are attributed to a singly and doubly negative charged C_{60}, respectively [17]. The spectral behaviour in Fig. 3 is interpreted as a one-step reduction from $C_{60} \rightarrow C_{60}^{2-}$ (1375 cm^{-1}).

In situ FTIR spectra taken during reduction of a hwbe C_{60} film in the presence of Li$^+$ (first cycle) are shown in Fig. 4.

Similarly to the reduction in TBA$^+$ containing electrolyte solution, a band at 1375 cm^{-1} occurs simultaneously with the decrease of the C_{60} band at 1428 cm^{-1}, indicating a one step reduction from $C_{60} \rightarrow C_{60}^{2-}$ in the first cycle. As has been shown in a previous paper [24], the individual reduction and reoxidation steps in higher cycle numbers are spectroscopically better resolved in the case of Li$^+$ compared to TBA$^+$. In situ FTIR spectra taken during reduction of a hwbe C_{60}

film in the presence of Li^+ (second cycle) are shown in Fig. 5.

The band at 1428 cm^{-1} from C_{60} changes in two consecutive steps, first to 1393 cm^{-1} and further to 1380 cm^{-1}, which indicates two different reduction processes, $C_{60} \rightarrow C_{60}^-$ at less negative potential values and C_{60} (or C_{60}^-) $\rightarrow C_{60}^{2-}$ [24] at more negative potentials.

From vapour phase doping experiments it has been reported that doping with Na^+ is different from the other alkali metals, because different structural phenomena occur [27]. The most stable reduction state of C_{60} in the Na–C_{60} system was found to be C_{60}^{2-} even though a stable NaC_{60} phase has also been reported [28]. In Fig. 6 the difference spectra during the reduction of a hwbe made film in the presence of Na^+ (first cycle) are shown.

The cyclic voltammetric response of the reduction of a C_{60} film in the presence of Na^+ is similar to the response in the presence of Li^+, one broad overlapping cathodic peak followed by two small anodic reoxidation peaks. However, in the FTIR spectra during electrochemical reduction in the presence of Na^+ an absorption peak at 1394 cm^{-1} occurs and remains unchanged even when higher negative potentials are applied. This peak is assigned according to the literature to the C_{60}^- phase [17].

The reduced species of C_{60} in the presence of K^+ and Rb^+ seem to be more soluble in acetonitrile and in the cyclic voltammetric experiments a current response from only one cycle was obtained. In situ FTIR difference spectra during electrochemical doping of C_{60} films in the presence of K^+ (hwbe film) are shown in Fig. 7. Spectral behaviour similar to the reduction in the presence of Li^+ and TBA^+ with a peak at 1375 cm^{-1}, interpreted to correspond to the C_{60}^{2-} phase, is seen. The small features at 1410 and 1450 cm^{-1} are probably due to spectral incompensation effects of the strong negative $F_{1u}(4)$ mode at 1428 cm^{-1} of C_{60}.

In the case of Rb^+ no redox reaction occurred in the case of hwbe films, probably due to the low concentra-
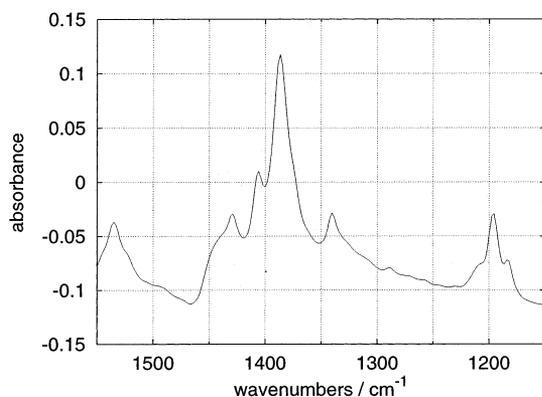
tion of the electrolyte salt in combination with the compact crystalline structure of the hwbe film. However, with solution cast films, redox reactions were observed also in 0.01 M $RbBPh_4$ + acetonitrile electrolyte solution. The intensity of the absorbance in the spectra is low due to the low amount of doped material obtained. The interference from the electrolyte solution is high and the peaks originating from either the salt or the solvent are marked in the spectra in Fig. 8.

In the presence of Rb^+ a broad absorption peak around 1365 cm^{-1} is formed upon reduction. The peak starts to develop from the beginning of the reduction at -700 mV simultaneously as a negative peak from C_{60} at 1428 cm^{-1} occurs. The broad peak results from overlapping of several bands at 1410, 1380, 1365 and 1350 cm^{-1}. The band at 1365 cm^{-1} has the highest intensity and has been assigned in the literature to C_{60}^{3-} salts [17]. The results indicate an electrochemical conversion of the C_{60} drop cast film into a mixed reduced state, mainly C_{60}^{3-}, but with contributions of 1–4 valent states.

3.3. Comparison of the rubidium vapour doped and the electrochemically doped C_{60}

The RbC_{60} phase, produced by vapour doping, has an exceptionally high stability, which has been explained by a polymeric crosslinking between C_{60} molecules [5]. The polymeric phase is reported to be created upon slow cooling to room temperature and is fully stable in air. Rapid quenching to temperatures below room temperature results in dimer formation [10]. To study whether it is possible to obtain the stable RbC_{60} phase also by electrochemical doping, in situ spectra of the rubidium doped C_{60} film were compared with a spectrum taken ex situ of a vapour doped C_{60} film. A spectrum of the RbC_{60} polymeric phase, made by vapour doping of a hwbe C_{60} film, is shown in Fig. 9.

Weak bands at 1428 and 1182 cm^{-1} from C_{60} can still be seen in the spectrum. The dominating peak at 1385 cm^{-1} and the small peaks at 1405 and 1341 cm^{-1} are assigned to originate from a split of the $F_{1u}(4)$ mode, characteristic for the polymeric RbC_{60} phase [11,29–31]. The $F_{1u}(3)$ mode is shifted to 1196 cm^{-1}. New peaks are seen in addition to the modes assigned to F_{1u} due to the lowering of the symmetry in a linear chain structure [11]. In comparison to the spectra from the electrochemically doped film (Fig. 8), the characteristic features of the vapour doped material are absent in the electrochemically doped film. From the spectral behaviour it can be concluded that the same RbC_{60} phase as obtained by vapour doping is not reproduced by electrochemical doping.

In addition to the doping experiments of pristine C_{60}, as described above, dedoping of vapour phase pro-

Fig. 9. FTIR spectrum of the RbC_{60} polymeric phase, made by vapour doping of a hwbe C_{60} film.

duced RbC_{60} was tried. The vapour doped film was used as the working electrode in an electrochemical cell containing 0.01 M $RbBPh_4$ + acetonitrile solution and a reoxidation back to C_{60} was tried without success in breaking the initial phase. No redox response could be obtained upon further reduction of the RbC_{60} film either, which again shows the exceptionally high stability of the vapour doped RbC_{60} phase.

3.4. Spectral effects of symmetry breaking

In all difference spectra obtained in situ during electrochemical reduction of C_{60} films (Figs. 3–8), additional FTIR bands arising in the region 1450–1500 cm^{-1} can be seen. A reversible band at 1466 cm^{-1} occurs independently of the cation used for doping. For pristine C_{60} a characteristic totally symmetric A_g pinch mode at 1469 cm^{-1} is reported in the Raman spectra [32]. Upon reduction, this band is shifted towards lower wavenumbers. This effect was suggested to arise from symmetry lowering due to surface interactions as well as to a Jahn–Teller distortion [33]. The Jahn–Teller distortion localizes the unpaired electrons in the equatorial region of the C_{60} structure that is slightly stretched along the principal axis leading to an ellipsoidal distortion [34]. Considering the symmetry lowering it seems likely that some typical Raman bands, especially the pinch mode at 1469 cm^{-1}, become visible in the FTIR spectra during reduction [35]. Other reactions taking place during reduction that can also give rise to additional spectral features are structural changes in the film created during doping [36] or the formation of the dimer of C_{60}^- as proposed in Ref. [37].

4. Summary

The in situ FTIR experiments show that the $F_{1u}(4)$ mode of solid C_{60} is highly dependent on the structure and on the degree of charging. Depending on the cation present, different reduction states of hwbe films of C_{60} are obtained within a similar potential range. In the case of Li^+, K^+ and TBA^+ the C_{60}^{2-} phase is obtained either in one or in two steps. With Na^+ only C_{60}^- is found. In the case of Rb^+ only a drop cast film could be studied and a mixed state of reduction states 1–4 was obtained. The same stable phase RbC_{60} as obtained by vapour phase doping of C_{60} films could not be achieved by electrochemical doping. In the electrochemically reduced C_{60} films, reversible peaks at 1455–1469 cm^{-1} are seen during reduction and reoxidation. The peaks are always much weaker than the shifted F_{1u} modes. The band around 1460 cm^{-1} is suggested to be due to symmetry lowering in the C_{60} molecule related to the negative charge on the molecule (charge induced Jahn–Teller distortion). Because of the lower symme-

try, Raman active bands become visible in IR. Other possible reasons for the extra peaks in the spectra of the reduced form of C_{60} are from the polymeric phase reported to be formed upon reduction.

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