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Infrared study of group V hexafluoride fullerides

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Abstract. Compounds of C_{60} and hexafluoride ions of group V elements (P, As, Sb) were studied by infrared spectroscopy. $C_{60}(AsF_6)_{1.9}$ was formed by reacting C_{60} powder with AsF_5 gas dissolved in liquid SO_2 . The AsF_6^- ion was identified by a broad ν_3 absorption at 703 cm^{-1} , a shoulder at 681 cm^{-1} and evidence of the sharp ν_4 absorption just below 400 cm^{-1} in the infrared spectrum. The low-frequency modes of C_{60} at 527 and 576 cm^{-1} were unshifted in the reacted powder. The $T_{1u}(3)$ mode of C_{60} , at 1183 cm^{-1} , was accompanied by neighbouring absorptions at 1194 and 1206 cm^{-1} , which were assigned to splitting of the triply degenerate mode. Three strong broad peaks at 1549 , 1406 and 1322 cm^{-1} observed in the spectra were assigned to splitting of the threefold degenerate $T_{1u}(4)$ mode of pristine C_{60} at 1428 cm^{-1} . Heat treatments of the sample, with temperatures ranging up to 350°C , were performed to thermally decalate the sample and to aid in identifying the infrared modes. The PF_6^- ion, in the sample of C_{60} reacted with NO_2PF_6 in SO_2 , was observed in the IR spectra by the broad ν_3 absorption at 830 cm^{-1} and the sharp ν_4 absorption at 558 cm^{-1} . No strong absorption of NO_2^- at 2360 cm^{-1} was observed, indicating that the sample was not a simple mixture of the two powders. The C_{60} absorption lines, at 527 , 576 , 1183 and 1428 cm^{-1} , were unshifted. However, the $T_{1u}(4)$ mode at 1428 cm^{-1} showed asymmetric broadening on the low-frequency side and small absorptions flanking the $T_{1u}(4)$ mode. These features, although much less pronounced, may correspond to the shifting and splitting observed in the $T_{1u}(4)$ mode of the $C_{60}(AsF_6)_{1.9}$ compound. The octahedral SbF_6^- ion was identified in the sample of C_{60} powder reacted with NO_2SbF_6 by the strong ν_3 absorption at 660 cm^{-1} . The C_{60} lines were unshifted, but small absorptions flanking the $T_{1u}(4)$ mode were again similar to the absorptions assigned to splitting in the $C_{60}(AsF_6)_{1.9}$ compound.

1. Introduction

The intercalation of alkali metal donors in C_{60} solid has been well established. In these materials, the alkali metal ions fit into the large octahedral and tetrahedral sites of the fcc lattice. These compounds exhibit almost complete charge transfer, leaving the C_{60} molecule in a negatively charged state. The discovery of superconductivity in potassium doped C_{60} at 18 K [1] resulted in a large amount of condensed matter research.

The low ionization potential of the C_{60} molecule also suggests intercalation of the solid with acceptor molecules but few of these materials have been reported. A good candidate for an electron acceptor in C_{60} , arsenic pentafluoride, has been found to react with graphite to form graphite intercalation compounds with electrical conductivity as high as that of silver. A reaction between C_{60} and AsF_5 was first reported in 1994 [2]. The material was characterized by x-ray diffraction, mass spectrum analysis and nuclear magnetic resonance. The new compound, like the alkali metal fullerides, was observed to be air sensitive making study of the material somewhat difficult. The study of the infrared (IR) spectra of the material, using a sealed cell with KBr windows to contain the air sensitive sample, revealed

a large absorption at 702 cm^{-1} , characteristic of the AsF_6^- ion. This led to a proposed composition of $\text{C}_{60}(\text{AsF}_6)_{1.9}$ [3]. However, use of the sealed cell was hindered by low transmission and only two of the four absorption lines from C_{60} were resolved clearly enough to report. Even with evidence from the other techniques, the existence of the compound was called into question due to the poorly resolved C_{60} lines in the IR spectra.

The main objective of this research project was to acquire further evidence supporting the existence of this C_{60} acceptor material. This consisted of acquiring infrared transmission spectra of the $\text{C}_{60}(\text{AsF}_6)_{1.9}$ compound using a specially constructed apparatus to contain the air sensitive samples. Also, in an attempt to drive off the intercalant, heat treatments of the sample up to 350°C were performed in vacuum before measurements at room temperature.

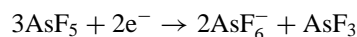
Reactions were also carried out in an attempt to intercalate solid C_{60} with other group V hexafluoride ions. It was realized that both the ν_3 and ν_4 modes of the octahedral PF_6^- ion could be observed within the range of the Fourier transform spectrometer, making identification of the ion facile. Thus, a reaction was implemented by combining C_{60} and NO_2PF_6 powders in SO_2 , a common polar solvent. A similar reaction was also conducted using NO_2SbF_6 . After removing excess NO_2 salt and drying, the powders were studied.

A review summarizing the status of the application of IR spectroscopy to the field of fullerene science, concentrating primarily on pristine and alkali metal doped C_{60} , is presented by Kuzmany *et al* [4]. In terms of other relevant solid state properties, the intermolecular bonds in the fcc lattice of C_{60} are largely van der Waals in nature, while the intramolecular bonds are covalent.

2. Experimental details

A solid solution method using AsF_5 gas, dissolved in SO_2 , reacted with C_{60} powder was utilized in order to prepare a homogeneous compound. The dark-brown C_{60} powder was observed changing to a green-coloured suspension after a few hours, with the complete reaction taking place, with continuous stirring, over several days. The excess SO_2 and AsF_5 were decanted and condensed leaving a dried powder with a uniform dark-green colour.

The reaction of AsF_5 forms AsF_6^- through the reaction



which has been established for the formation of $\text{Hg}_3(\text{AsF}_6)_2$ [5]. Here, the AsF_5 oxidizes C_{60} to form AsF_6^- and to maintain charge neutrality of the compound, as the transparent AsF_3 liquid is decanted with the SO_2 .

The process of synthesizing the phosphorus and antimony hexafluoride fullerenes was conducted in a slightly different manner. PF_5 is a colourless gas which reacts immediately with water, thus any moisture would generate HF. It is also a weaker Lewis acid than AsF_5 . Thus, for ease and safety of handling, and to initiate a reasonable reaction time, the hexafluoride salt, NO_2PF_6 , was employed as a direct source of PF_6^- ions. In the glove box, 500 mg C_{60} was combined with a stoichiometric amount of NO_2PF_6 (using a 1:2 ratio as suggested by $\text{C}_{60}(\text{AsF}_6)_{1.9}$). The powders were thoroughly mixed using a mortar and pestle and transferred to a Pyrex H-shaped reaction vessel which made it possible to decant the SO_2 after the reaction. It had a distinctive brown tinge indicative of dissolved NO_2 .

The sample was removed in an inert atmosphere for study. A reaction using NO_2SbF_6 was performed in a similar manner, with a brown colour observed in the liquid SO_2 . Exposing part of the sample to room atmosphere indicated air sensitivity, as it changed to a brown colour. Thus, all handling of the samples was conducted in an argon dry box.

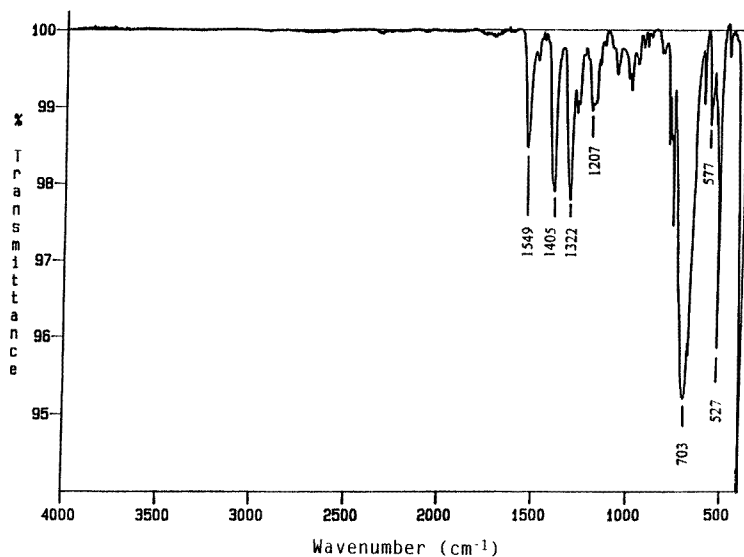


Figure 1. The Fourier transform infrared spectrum of $C_{60}(AsF_6)_{1.9}$.

A Bio-Rad FTS-40 Fourier transform system was used with a ceramic source for measurements between 400 and 4000 cm^{-1} . The sample material was combined with potassium bromide (Aldrich, FT-IR grade 99+%) using a mortar and pestle, then pressed into a pellet using a stainless steel pellet press. All samples were treated as air sensitive and were handled in an argon glove box. Transportation of the pellet from the glove box to the FTS sample chamber was performed with the sample in a stainless steel cylinder sealed to the base with a rubber O-ring. The cylinder was raised when the sample holder was in the compartment of the Fourier transform spectrometer which had been flushed with dry nitrogen.

Thermal decalation of the samples was performed with the powder contained in a Pyrex reaction vessel (which was previously heat treated under vacuum to remove moisture). After 30 min, the oven was removed to allow the sample to cool to room temperature. The reaction vessel was then sealed and transported back to the argon dry box in preparation for infrared measurements.

3. Experimental results

The Fourier transform infrared spectrum of the $C_{60}(AsF_6)_{1.9}$ powder, shown in figure 1, over the range $4000\text{--}400\text{ cm}^{-1}$, reveals a number of features. The large broad absorption centred at 703 cm^{-1} was assigned to the ν_3 vibration of the AsF_6^- ion. The $T_{1u}(1)$ and $T_{1u}(2)$ modes of C_{60} , at 527 and 577 cm^{-1} , are unshifted in frequency. The $T_{1u}(3)$ mode of C_{60} , at 1183 cm^{-1} , appears somewhat obscured by other features. There are three strong peaks, similar in intensity and width, at 1549 , 1405 and 1322 cm^{-1} , in the region of the $T_{1u}(4)$ line of pristine C_{60} at 1428 cm^{-1} .

Successive heat treatments of the sample were performed in vacuum at different temperatures in an attempt to decalate the sample and aid in identification of the modes. Heat treatments up to 150°C resulted in little change in the infrared spectrum of the $C_{60}(AsF_6)_{1.9}$. However, progressive treatments up to 350°C resulted in a decrease in the intensity of the

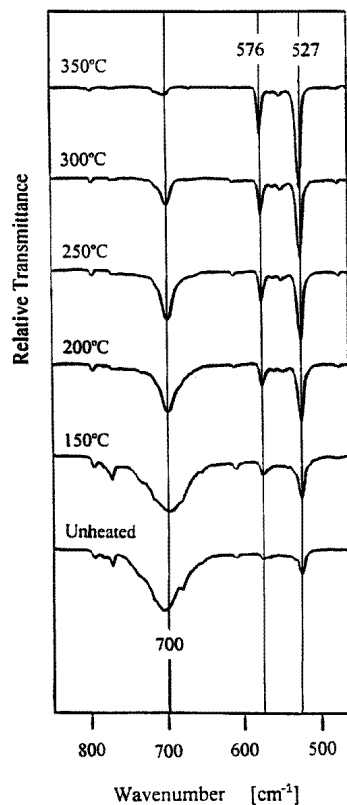


Figure 2. Successive heat treatments of $C_{60}(AsF_6^-)_{1.9}$ showing a decrease in the AsF_6^- absorption, near 700 cm^{-1} and the increase of the relative strength of the C_{60} lines in the IR spectra.

703 cm^{-1} line and an increase in the relative strength of the C_{60} lines at 527 and 576 cm^{-1} (figure 2). The decrease in intensity of the three lines, at 1549 , 1405 and 1322 cm^{-1} , and the emergence of the absorption at 1429 cm^{-1} with heating (figure 3), suggest that the triplet may be due to symmetry breaking of the triply degenerate $T_{1u}(4)$ mode. The emergence of sharply defined absorption lines at 527 , 576 , 1183 and 1429 cm^{-1} implies that the sample reverts back to the initial C_{60} starting material. These four strong C_{60} lines indicate that the buckyballs stay intact during the intercalation and decalation of the sample.

The successful decalation of the $C_{60}(AsF_6^-)_{1.9}$ sample was supported by x-ray diffraction analysis which showed the return of the fcc C_{60} lattice structure after heat treatment from the body-centred tetragonal lattice of the arsenic hexafluoride fulleride [2].

The infrared spectrum of the C_{60} powder reacted with NO_2PF_6 in liquid SO_2 is shown in figure 4. While the high frequency portion of the spectrum, which is not shown, is completely bare, the low-frequency portion has quite a number of absorption regions. The broad ν_3 absorption of PF_6^- , reported by Begun and Rutenberg [8] at 830 cm^{-1} , is observed as well as the sharp ν_4 mode reported at 558 cm^{-1} (seen here at 559 cm^{-1}). The C_{60} lines in the spectrum appear unshifted. Heat treatment of the PF_6^- compound at 350°C under vacuum yielded an IR spectrum that was similar to that of C_{60} .

The IR spectrum of the C_{60} powder reacted with NO_2SbF_6 is shown in figure 5. The strong broad absorption of SbF_6^- at 660 cm^{-1} is clearly visible. The C_{60} peaks are unshifted, but again there are similarities with the previous spectra. The inset of figure 5 shows the region surrounding the $T_{1u}(3)$ and $T_{1u}(4)$ lines.

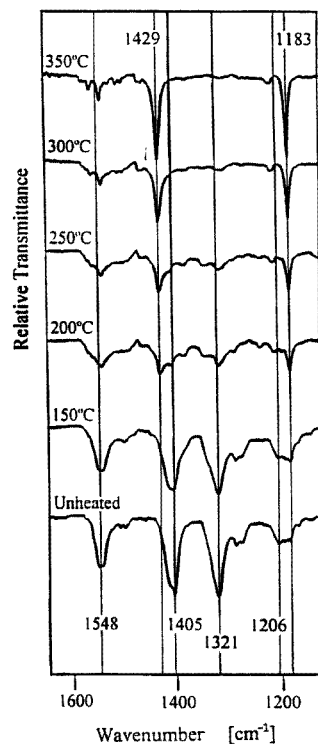


Figure 3. The 1405 cm^{-1} line shifts to 1429 cm^{-1} with increased heating, as the proposed triplet fades away. The emergence of the 1183 cm^{-1} line also indicates the return of undoped C_{60} with successive heat treatments.

4. Discussion

The region of interest, $1700\text{--}400\text{ cm}^{-1}$, in $\text{C}_{60}(\text{AsF}_6)_{1.9}$ is shown in figure 6. The absence of the very strong stretching modes at 811 and 787 cm^{-1} of the trigonal-bipyramidal AsF_5 molecule suggests that there are few, if any, of the reactant molecules trapped in the sample. The octahedral AsF_6^- molecule has six normal modes of vibration, illustrated in figure 7. Vibrations ν_3 and ν_4 are infrared active. The inset of figure 6 shows the infrared spectrum obtained by Naulin and Bougon [6] for the dioxygenal salt $\text{O}_2 + \text{AsF}_6^-$ showing the two absorption lines at 700 and 385 cm^{-1} assigned to the ν_3 and ν_4 modes of the AsF_6^- ion (these modes were also observed by Begun and Rutenberg [8] at 699 and 392 cm^{-1}). Naulin and Bougon also discuss an observed shoulder at about 680 cm^{-1} on the $\nu_3[\text{T}_u]$ IR absorption band, which was assumed to be due to a ν_3 splitting. This shoulder, on the strong broad 703 cm^{-1} absorption, also appears in the $(\text{AsF}_6)_{1.9}\text{C}_{60}$ spectrum at 681 cm^{-1} . Unfortunately, the ν_4 absorption line of the AsF_6^- ion, at 385 cm^{-1} , lies just beyond the range of the spectroscope, yet evidence of this peak may appear at the low-frequency end of the spectrum because the absorption at, or just below, 400 cm^{-1} decreases in size at approximately the same rate as the ν_3 mode at 703 cm^{-1} after thermal decalation. Thus, the observation of the strong ν_3 absorption at 703 cm^{-1} , the 681 cm^{-1} shoulder, and the absorption near 400 cm^{-1} identify the AsF_6^- ion in the sample.

Due to the similarities in strength and breadth of the absorptions at 1322 , 1405 and 1549 cm^{-1} in $\text{C}_{60}(\text{AsF}_6)_{1.9}$, as well as their uniform changes on heating, these modes have been assigned to the splitting of the triply degenerate $\text{T}_{1u}(4)$ mode of pristine C_{60} . The possible line splitting in the $\text{T}_{1u}(4)$ mode, and the absence of splitting in the lower-frequency modes, is intriguing because all the modes have the same symmetry, but a similar

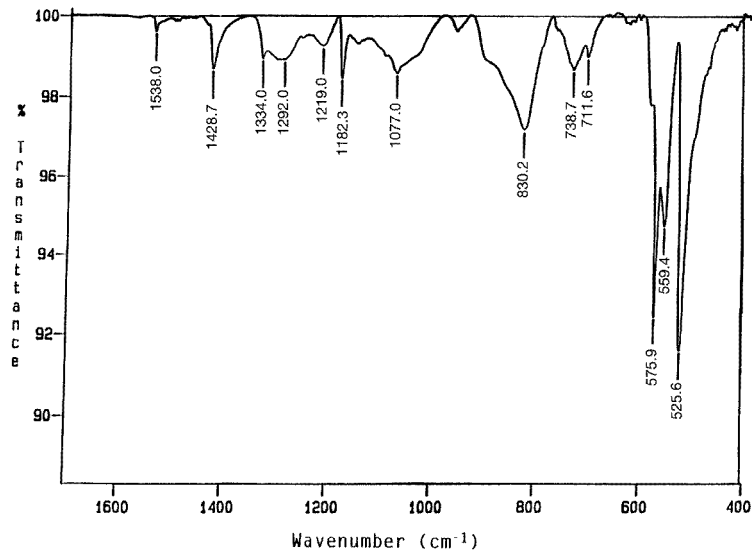


Figure 4. The IR spectrum of C_{60} powder reacted with NO_2PF_6 ($400\text{--}1700\text{ cm}^{-1}$), showing the broad ν_3 and the sharp ν_4 absorption, at 830 and 559 cm^{-1} , respectively, of the octahedral PF_6^- ion.

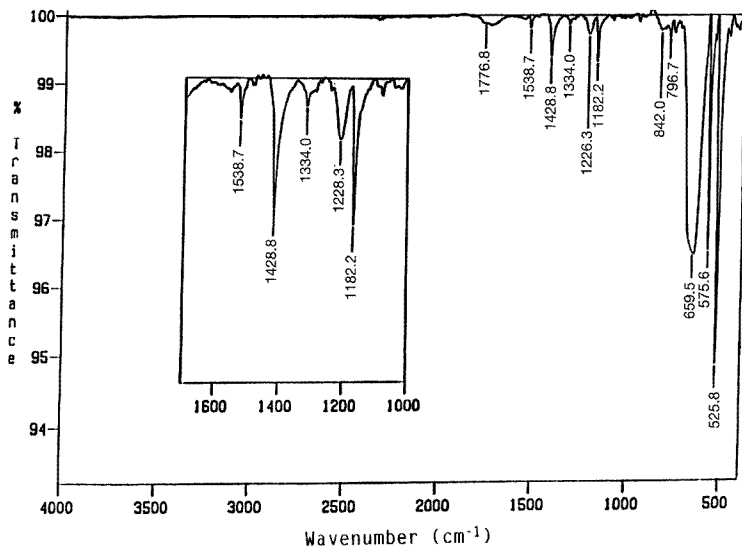


Figure 5. The IR spectrum of C_{60} powder reacted with NO_2SbF_6 showing the broad ν_3 absorption of the SbF_6^- ion at 659 cm^{-1} . The inset shows the region surrounding the $T_{1u}(3)$ and $T_{1u}(4)$ modes of C_{60} .

occurrence has been observed, to a much smaller degree, even in the undoped material as it is cooled through the orientational phase transformation. Narisimham *et al* [9] observed the IR absorption at 1183 cm^{-1} to narrow and shift slightly towards higher energy while the mode at 1429 cm^{-1} split into three lines, separated by only a few wavenumbers, below

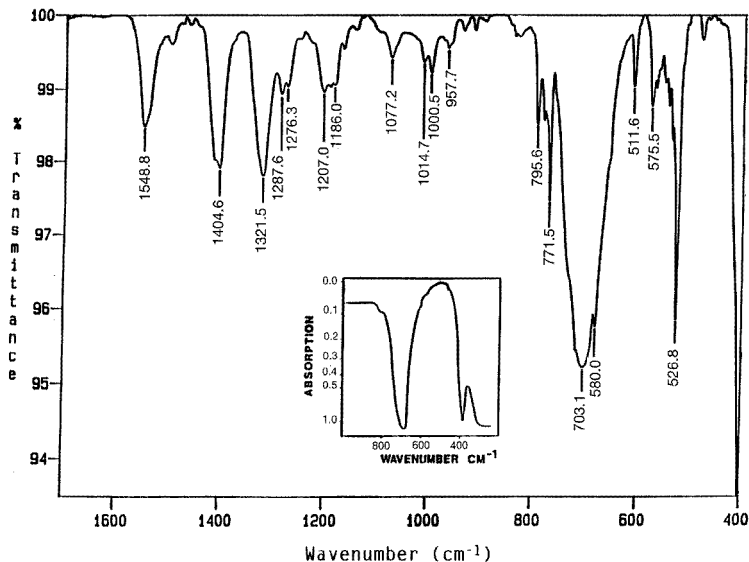


Figure 6. The IR spectrum in the range 400–1700 cm⁻¹ for C₆₀(AsF₆⁻)_{1.9}. The inset shows the ν₃ and ν₄ absorptions of the AsF₆⁻ ion [8].

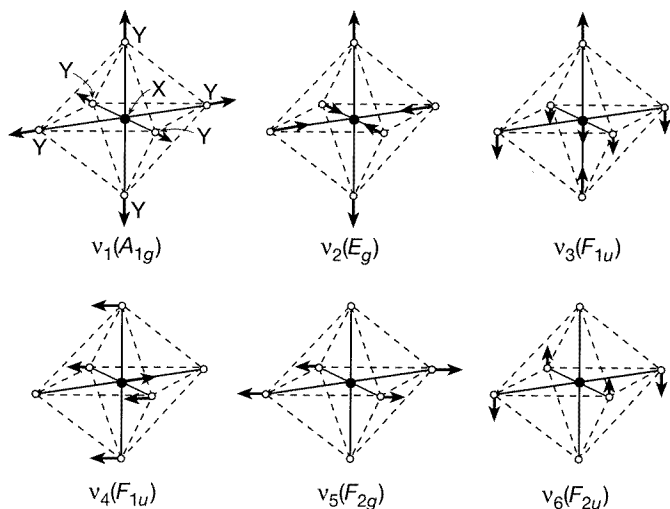


Figure 7. The six normal modes of vibration of the octahedral XF₆⁻ ions (where X = P, As and Sb). The ν₃ and ν₄ vibrations are infrared active.

245 K in pristine C₆₀ films. These splittings were not expected *a priori* because unsplit the T_{1u} modes are supported in both space groups (*Fm3m* and *Pa3*). They declared that the observed splitting pattern must therefore be related to changes in the local crystal field (i.e. differences in interball coupling) which arise when the solid C₆₀ enters a rotationally locked phase.

The splitting of the T_{1u}(4) mode in our samples is huge (over 100 wavenumbers) and

appears much too large to be explained just by symmetry reduction of the crystal field. Indeed, a total splitting of the $T_{1u}(4)$ mode of 65 cm^{-1} was observed in Rb_1C_{60} , with no splitting of other modes, and was suggested to be due to some chemical deformation of the C_{60} molecules, such as that arising from cycloaddition bonding [10]. Regardless of the possible splitting, there is a definite shift of the $T_{1u}(4)$ line of pristine C_{60} at 1428 cm^{-1} , to 1405 cm^{-1} in the doped $\text{C}_{60}(\text{AsF}_6)_{1.9}$ sample. Large shifts in the positions of the lines have also been observed in other doped compounds, including an observed shift of 88 cm^{-1} in the $T_{1u}(4)$ mode of a K_6C_{60} film [11], which was suggested to be due to a charged phonon effect.

The $T_{1u}(3)$ mode of C_{60} is observed in the $\text{C}_{60}(\text{AsF}_6)_{1.9}$ compound crowded by higher-frequency features. The triplet at 1206 , 1194 and 1183 cm^{-1} , with all lines of approximately the same strength, may represent splitting of the triply degenerate mode. The pristine C_{60} mode, at 1183 cm^{-1} , becomes more dominant as the sample is thermally decalated (shown in figure 3).

A second possible explanation is that the $T_{1u}(3)$ line shifts to higher frequencies due to intercalation, yet the three closely spaced absorptions may be contributions from more than one phase in the IR spectrum, which are present due to non-uniform intercalation. In this case the observation of the three closely spaced absorptions, which shift in strength towards the lowest frequency with thermal decalation, may indicate a correspondence to three distinct phases in the sample (presumably $\text{C}_{60}(\text{AsF}_6)_x$ with $x = 2, 1, 0$). This second hypothesis is less likely considering that the 1428 cm^{-1} line in pristine C_{60} ($x = 0$ phase) is not observed in the $\text{C}_{60}(\text{AsF}_6)_{1.9}$ spectra.

The infrared spectrum of the C_{60} powder reacted with NO_2PF_6 in liquid SO_2 shows a number of features in the low-frequency portion of the spectra. The PF_6^- ion in the sample is identified by the broad ν_3 absorption [8], at 830 cm^{-1} , and the sharp ν_4 mode reported at 559 cm^{-1} . Also, it should be noted that neither the strong absorption at 2360 cm^{-1} nor the weaker absorption at 570 cm^{-1} [7] of NO_2^+ are observed, indicating that the powder is not a simple mixture of NO_2PF_6 and C_{60} . The NO_2 gas observed during the reaction process indicated that the NO_2^+ ions, dissociated in the liquid SO_2 , had oxidized the C_{60} molecules. Lines in the IR spectrum appear at 526 , 576 , 1182 and 1429 cm^{-1} , unshifted from those of C_{60} , but the $T_{1u}(4)$ line is flanked by two neighbouring absorptions, at 1538 and 1334 cm^{-1} , that are close in frequency to the observed lines at 1549 and 1322 cm^{-1} in $(\text{AsF}_6)_{1.9}\text{C}_{60}$. Although the $T_{1u}(4)$ mode remains at 1429 cm^{-1} , it appears asymmetrically broadened on the lower-frequency side, which may correspond with the observed downshift of this line in the arsenic hexafluoride sample. These features are similar to those observed with the intercalation of the AsF_6^- ion, but are not nearly as pronounced. Heat treatment of the PF_6^- compound at 350°C under vacuum yielded an IR spectrum with strong absorptions at 526 , 576 , 1182 and 1429 cm^{-1} . These values, close to those of pristine C_{60} , combined with the disappearance of lines attributed to PF_6^- , indicated the decalation of the sample, with no disruption of the buckyball.

The reaction with NO_2SbF_6 and C_{60} shows no absorption due to the NO_2^+ ion at 2360 or 570 cm^{-1} [7] in the IR spectrum. It does, however, show the strong broad absorption of SbF_6^- at 660 cm^{-1} which is very close (for such a broad peak) to the reported value of 669 cm^{-1} [8]. The ν_4 mode of SbF_6^- , at 350 cm^{-1} , lies below the range of the spectrometer. Again, the observed lines of the hexafluoride anion, without the NO_2^+ ion, indicate that the resulting powder is not simply a mixture of C_{60} and NO_2SbF_6 . Although the C_{60} peaks are unshifted, the $T_{1u}(3)$ line, at 1182 cm^{-1} has a higher-frequency counterpart at 1226 cm^{-1} and the $T_{1u}(4)$ line is flanked by absorptions at 1538 and 1334 cm^{-1} . These features, although small, may correspond to the splitting observed in the high-frequency modes of

(AsF₆)_{1.9}C₆₀. Heat treatment of the powder at 350 °C led to an IR spectrum that was very similar to that of pristine C₆₀, indicating the decalation of the sample, with no disturbance of the molecule.

There is no evidence in the IR spectra to suggest the presence of SO₂ solvent, which has absorptions at 1147, 517 and 1351 cm⁻¹ [12], in the samples. Moreover, the 739 cm⁻¹ [13] absorption line of the stable AsF₃ molecule is not observed in the C₆₀(AsF₆)_{1.9} sample. The AsF₃ molecule also has absorptions at 262, 337 (below the range of the spectrometer) and 699 cm⁻¹ (close to the observed line attributed to AsF₆⁻).

Differences in the lattice dynamics between the fullerides and the fullerite may arise from a number of factors. The introduction of ions into the interstitial sites changes the crystal structure and symmetry and may give rise to new optic modes. New phonon modes are discussed by Dresselhaus *et al* [14] for doped C₆₀ in the space groups T_h⁶ (fcc) and T_h⁵ (bcc). However, the body-centred tetragonal phase, clearly observed in the (AsF₆)_{1.9}C₆₀ compound, is a lower-symmetry space group (where the C₆₀ molecules would occupy sites with C_{2v} symmetry), and is only briefly mentioned in the paper.

Another important factor is the charge transfer from the molecule to the acceptor ions, which will alter the bond bending and bond stretching force constants. This may explain why the higher-frequency T_{1u}(3) and T_{1u}(4) infrared modes of C₆₀ are affected by the intercalation of the ions, while the lower ones are not. The tangential motion of the carbon atoms, in the higher-frequency modes, stretches and bends the bonds to a greater degree than the progressively more radial motion of the lower-frequency modes.

Additional features in many of the alkali metal fullerides have been assigned to IR forbidden and second-order modes which have become IR active due to charge transfer (which can dress many of the modes with a dipole moment). Martin *et al* [15] illustrated how the addition (or reduction) of electrons to a complex molecule can enhance the strength of a 'silent' IR active phonon. However, as long as only symmetric electronic states are allowed, the mode is 'silent' since there is no net dipole moment in the direction of the electric field. Asymmetric states are allowed with electron transfer between the two pairs of atoms which couples to the atomic displacements through the rearrangement of electronic states and generates an electric dipole moment. Rice and Choi [16] formulated a model in which coupling can even dress *gerade* (symmetric) modes with a dipole moment, a behaviour which is well known for organic charge transfer systems. This model was used to describe the IR spectra of the K₃C₆₀ compound, in which observed features were assigned to the *gerade* modes of A_g and H_g symmetry [11]. The majority of the fundamental modes are not optically active in pristine C₆₀ and consequently cannot be directly observed. Although some assignments of absorption features in (AsF₆)_{1.9}C₆₀ can be speculated (such as the sharp line at 772 cm⁻¹ lying very close to the H_g(4) mode observed at 774 cm⁻¹ in the Raman spectra), a more detailed analysis is not only in principle very complicated but also inappropriate, as shifts of Raman active modes, and theoretical shifts of optically inactive modes, have not been studied for acceptor intercalated C₆₀ materials.

5. Conclusions

The study of the IR spectra of the C₆₀(AsF₆⁻)_{1.9} compound during thermal decalation, has confirmed the existence of this C₆₀ compound intercalated with acceptor molecules. IR spectroscopy also yielded strong evidence for the interaction of C₆₀ with other group V hexafluoride ions, PF₆⁻, and SbF₆⁻.

The broad ν₃ absorption at 703 cm⁻¹, as well as a shoulder at 680 cm⁻¹, and evidence of the sharp ν₄ absorption just below 400 cm⁻¹ identifies the octahedral AsF₆⁻ ion in the

sample of C_{60} reacted with AsF_5 . The low-frequency $T_{1u}(1)$ and $T_{1u}(2)$ modes of C_{60} , at 527 and 576 cm^{-1} , in the IR spectra of the samples appear unaffected by intercalation. The $T_{1u}(4)$ mode of the $(AsF_6)_{1.9}C_{60}$ exhibits a downshift in frequency from the 1428 cm^{-1} absorption line of pristine C_{60} to 1406 cm^{-1} . Moreover, this triply degenerate mode exhibits splitting leading to neighbouring peaks at 1549 and 1322 cm^{-1} . Three closely spaced peaks at 1206, 1194 and 1183 cm^{-1} are tentatively assigned to splitting of the T_{1u} mode. Thermal decalation of the $C_{60}(AsF_6)_{1.9}$ sample performed with temperatures ranging up to 350 °C results in the emergence of the strong C_{60} lines in the infrared spectra, at 527, 576, 1183 and 1429 cm^{-1} , indicating that the buckyball has retained its molecular identity throughout the intercalation and decalation processes.

In the sample of C_{60} reacted with NO_2PF_6 , there exist both the broad ν_3 absorption of the octahedral PF_6^- ion at 830 cm^{-1} and the sharp ν_4 line at 558 cm^{-1} . The absence of the broad absorption of NO_2^- indicates that the sample was not a simple mixture of the two powders. Small absorptions at 1539 and 1334 cm^{-1} flanking the $T_{1u}(4)$ mode, which also shows broadening on the low-frequency side, may correspond to the similar, but much enhanced, features in the $C_{60}(AsF_6)_{1.9}$ compound. Heat treatment of the powder at 350 °C leads to an IR spectrum very similar to that of pure C_{60} .

The presence of the SbF_6^- ion, in its respective sample, is identified by the strong ν_3 absorption at 660 cm^{-1} . Absorptions at 1539 and 1334 cm^{-1} , flanking the $T_{1u}(4)$ mode, are also seen in the IR spectra. Thermal decalation of the sample, identified by the return of the four strong C_{60} lines in the IR spectra, is achieved by heating to 350 °C in vacuum.

Acknowledgments

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