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Oxidation of C₆₀ by hexafluorides

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Abstract. Far infrared (FIR) and Raman spectroscopy studies of C₆₀(AsF₆)_x and C₆₀(SbF₆)_x were carried out at room temperature. The FIR spectra showed the presence of AsF₆⁻ and SbF₆⁻. There was a shift upward of (13 ± 3) cm⁻¹ in the tangential A_g mode compared to that of neutral C₆₀. This shift is attributed to a reduction in the electron screening of carbon. The charge transfer from C₆₀ is 0.033 electrons per carbon atom, which is equivalent to two electrons per C₆₀ molecule. This shows that the oxidation of C₆₀ in C₆₀(AsF₆)₂ and C₆₀(SbF₆)₂ is the source of the charge on the negative ions. The effect of air exposure on the compounds as indicated by the FIR spectra is also reported.

1. Introduction

Charge transfer of electrons to C₆₀ is well known in the compounds formed with the alkali metals. It is also established that some of the compounds are superconductors with critical temperatures between 18 K and 33 K [1–4]. Lewis acids have also been reacted with C₆₀ to form compounds. However, they exhibit only semiconducting behaviour and the oxidation of C₆₀ by the transfer of charge from it is more difficult to establish [5–12].

In graphite intercalation compounds, halogen atoms and halogen related molecules act as acceptors [13]. However, it is reported that the ionization potential of C₆₀ is more than 7 eV based on both calculations and experiments [14, 15]. Graphite is a semimetal with a work function of 5 eV and diamond is a semiconductor with an ionization energy of about 10 eV and an electron affinity of 5 eV. C₆₀ can be viewed as a mixture of graphite and diamond in the sense that it contains both sp² and sp³ hybridization, which lowers the valence band top compared with the eigenvalue of the p orbital. Thus, C₆₀ has a higher electron negativity, which makes hole injection in the valence band of C₆₀ difficult. However, we show in this work that charge is removed from C₆₀ in the formation of compounds from AsF₅ and SbF₅.

There are two groups of phonon modes in C₆₀: a group of high-frequency, mainly tangential modes and a group of lower-frequency modes with radial character [16]. Raman scattering studies [17] of alkali-metal C₆₀ compounds showed that the high-frequency, tangential modes soften relative to those in C₆₀ and the frequency decreases by about 1.5–3%. It was shown by Jishi and Dresselhaus [18] that the charge transfer from the alkali-metal atoms to the C₆₀ molecules results in the lowering of the high-frequency tangential mode in good agreement with the Raman experimental results.

The C₆₀ compounds that have been formed with Lewis acids include C₆₀(SbCl₅)_x, C₆₀(AsF₆)_x, C₆₀(SbF₆)_x, C₆₀(PF₆)_x, C₆₀(InCl₃)_x, C₆₀(AlCl₃)_x and C₆₀(FeCl₃)_x [5–12]. Far-infrared absorption showed that there was interaction between the molecules and carbon and that there were ions AsF₆⁻, SbF₆⁻ and PF₆⁻. The conductivities of most of them had the

properties of a semiconductor. A weight analysis of $C_{60}(AsF_6)_x$ compared with the weight of the components in the reaction showed that x is 1.9 and close to 2 in a fully reacted compound. X-ray diffraction studies showed that there is a body-centred-tetragonal unit cell in $C_{60}(AsF_6)_x$.

The origin of the charge on the hexafluoride ions has not been established previously. The purpose of this work is to show clearly from Raman and infrared spectroscopy measurements that there is charge transfer from the C_{60} molecule to AsF_6^- and SbF_6^- . Far-infrared spectroscopy is also used to show the effect of air exposure on the samples and x-ray diffraction shows that both compounds are crystalline.

2. Experimental details

$C_{60}(AsF_6)_x$ was prepared by a solid solution method with C_{60} powder and AsF_5 gas in liquid SO_2 at room temperature. The reaction time was 2 days, after which the SO_2 and excess AsF_5 were decanted and condensed, leaving a dry powder with a uniform dark-green colour. $C_{60}(SbF_6)_x$ was prepared by reacting a mixture of NO_2 , SbF_6^- and C_{60} powders with a molar ratio of 2:1 in liquid SO_2 . After the reaction, the SO_2 had a distinctive brown tinge, indicative of dissolved NO_2 and was decanted from the reaction vessel. All handling of the samples was done in a dry box filled with argon and samples were sealed in containers for the measurements.

A Bio-Rad FTS-40 Fourier transform system was used for measurements between 400 and 4000 cm^{-1} . A small amount of a sample mixed with potassium bromide was pressed into a pellet when they were in the dry box.

The Raman spectra were obtained at room temperature with an Ar-ion laser as part of a Jobin Yoon/TSA Mod S-3000 Raman spectrometer. The sample was in a sealed, Pyrex tube with an inside diameter of 1 mm.

The x-ray powder diffraction spectrum taken with $Cu K\alpha$ radiation of $C_{60}(SbF_6)_x$ consisted of Bragg diffraction at 13° , 19° and 20.5° . This shows that $C_{60}(SbF_6)_x$ is crystalline but does not allow a determination of the unit cell because there are not sufficient diffraction lines. However, the angles of the diffraction lines indicate that the unit cell is different from that of $C_{60}(AsF_6)_x$, which has a tetragonal unit cell [6]. The x-ray diffraction lines of $C_{60}(AsF_6)_x$ that were reported previously [6] were reproduced in this work. Thus both compounds have an ordered arrangement of molecules and are not simply a mixture of C_{60} and the hexafluoride.

3. Experimental results

Figure 1 is the far-infrared (FIR) spectrum of $C_{60}(AsF_6)_x$ in the range 400 cm^{-1} to 2000 cm^{-1} . It is similar to our previous work [9] and contains a strong absorption of AsF_6^- , low-frequency lines of C_{60} (527 and 576 cm^{-1}) and three high-frequency lines. There are small changes in the spectrum of a sample exposed to air for 5 min. The high-frequency lines are shifted from 2 to 14 cm^{-1} . In the spectrum of the sample exposed to air for one day shown in figure 2, the four C_{60} lines are evident. A very similar spectrum was obtained with a sample exposed to air for 3 d.

The FIR spectrum of $C_{60}(SbF_6)_x$ was very similar to the one published previously [9]. There was strong absorption from SbF_6^- at 660 cm^{-1} and there were four absorption lines from C_{60} with additional lines associated with the two high-frequency ones. Exposing the sample to air for 15 or 30 min weakened the absorption lines associated with the C_{60} lines and did not result in any other significant changes. With samples of $C_{60}(SbF_6)_x$ heated at 200, 300 and 400 $^\circ C$ in vacuum there was a white powder at the cold end of the reaction vessel due to sublimation from the sample. The FIR spectrum of the powder gave evidence of the existence of SbF_3 and $SbF_3 \cdot SbF_5$. Figure 3 shows the IR spectrum of a $C_{60}(SbF_6)_x$ sample, after it had

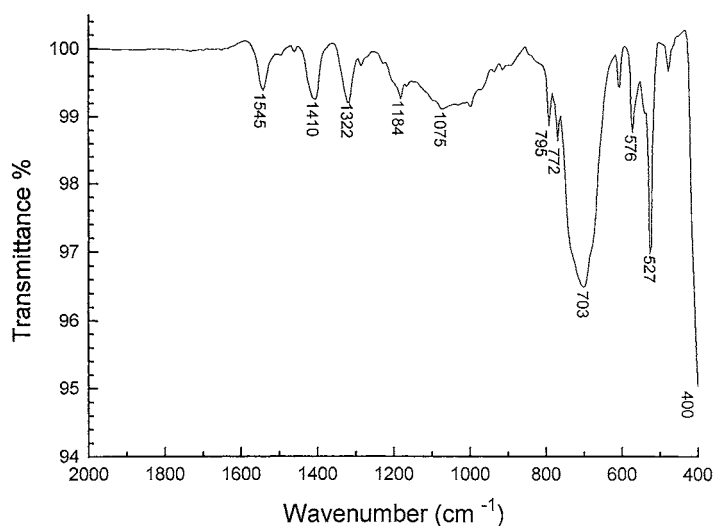


Figure 1. Far-infrared spectrum of $C_{60}(AsF_6)_x$ without exposure to air.

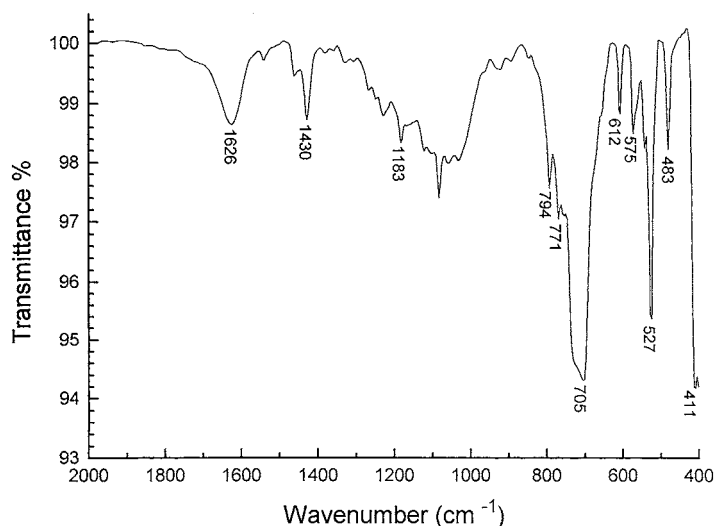


Figure 2. Far-infrared spectrum of $C_{60}(AsF_6)_x$ exposed to air for one day.

been heated at $400^\circ C$. There are four C_{60} lines and the broad line centred at 1131 cm^{-1} results from the C–F coupling and fits well with C–F stretching mode because it agrees with the FIR spectrum of fluorinated fullerenes with a broad absorption at 1165 cm^{-1} [19]. This coupling did not occur with $C_{60}(AsF_6)_x$ after it was heated.

The Raman spectroscopy measurements were made with laser powers of 1.2, 1.5, 10 and 60 mW. Use of the highest power resulted in a spectrum that was the same as the C_{60} spectrum to within several wavenumbers. It is apparent that the AsF_6^- and SbF_6^- were driven from the sample by a laser power of 60 mW. It was necessary, therefore, to use very low laser powers to obtain the spectra of the compounds. This provided results with quite a low signal-to-noise ratio and limited the study to the most intense Raman peaks.

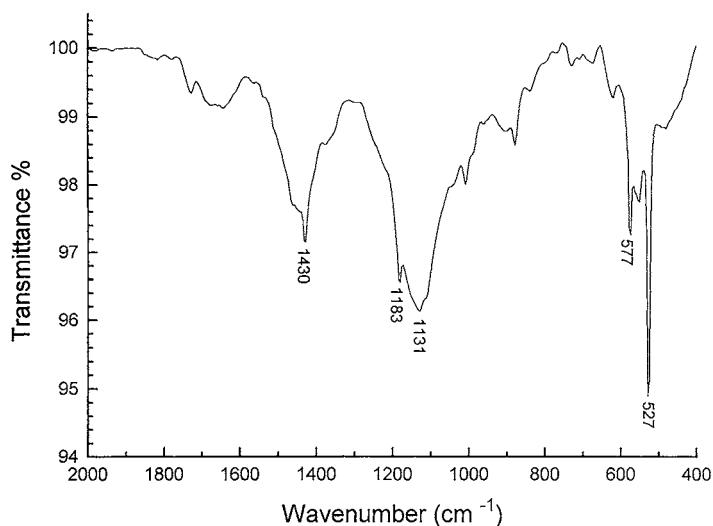


Figure 3. Far-infrared spectrum of $C_{60}(SbF_6)_x$ after it was heated at $400^\circ C$.

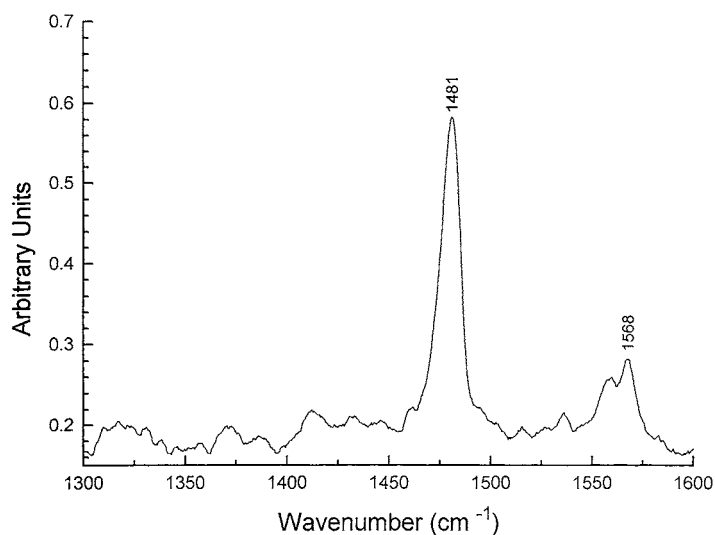


Figure 4. Raman spectrum of $C_{60}(AsF_6)_x$ taken with a laser power of 1.5 mW for the range $1300\text{--}1600\text{ cm}^{-1}$.

The Raman spectrum of $C_{60}(AsF_6)_x$ taken with a laser power of 1.5 mW is shown in figure 4. The A_g frequency is $(1481 \pm 1)\text{ cm}^{-1}$. The frequency of C_{60} from our measurements is $(1468 \pm 2)\text{ cm}^{-1}$. This indicates an upshift of $(13 \pm 3)\text{ cm}^{-1}$ in the compound. The C_{60} H_g frequencies 1568 cm^{-1} and 1422 cm^{-1} cannot be measured with sufficient accuracy to determine any shifts.

The Raman spectrum of $C_{60}(SbF_6)_x$ taken with a laser power of 10 mW is shown in figure 5. The A_g mode is split at frequencies of 1478 cm^{-1} and 1464 cm^{-1} . The two frequencies can be explained if the sample was decomposed partially by the laser beam. The frequency 1464 cm^{-1} is then attributed to the part of the sample in which the SbF_6 was removed because the frequency

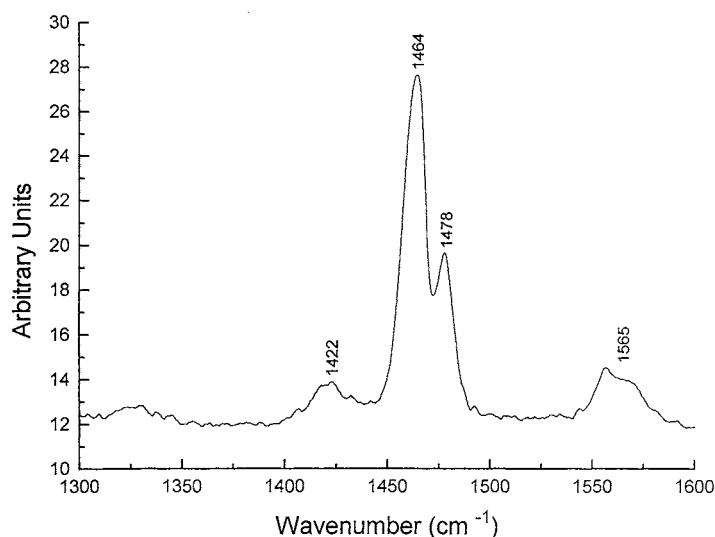


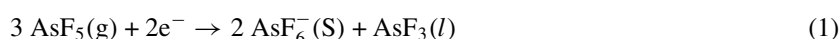
Figure 5. Raman spectrum of C₆₀(SbF₆)_x taken with a laser power of 10 mW.

is close to that of C₆₀. The frequency 1478 cm⁻¹ is attributed to the compound. This indicates an upshift of 14 cm⁻¹ in the compound. This interpretation is supported by the data taken with a laser power of 1.2 mW, which was the lowest power that was possible with stable operation of the laser. In figure 5 the amplitude of the upper-frequency peak is 53% of the amplitude of the lower-frequency one. This percentage was increased to 81% with the use of a laser power of 1.2 mW. This increase is attributed to less sample decomposition with the lower laser power so that the higher-frequency peak from the compound is relatively larger.

In figure 5, the H_g frequencies 1422 cm⁻¹ and 1565 cm⁻¹ are close to the corresponding ones of C₆₀. The lines are too broad to allow the determination of any shifts of the frequencies.

4. Discussion

The reaction in the formation of AsF₆⁻ from AsF₅ is



with a similar reaction for SbF₅. The spectrum in figure 1 clearly shows the presence of AsF₆⁻ by the lines at 703 cm⁻¹ and just below 400 cm⁻¹. The frequencies from SbF₆⁻ are also identified in the spectrum of SbF₆⁻ [9]. Thus, there is direct evidence of AsF₆⁻ and SbF₆⁻ in the compounds. There is also evidence of the second product SbF₃ in the powder derived from a heated sample. Thus, the source of the electrons in (1) is important to establish.

Evidence of the source of the electrons in (1) can be obtained from the Raman results. There is an upshift in the frequency of the higher A_g mode from the C₆₀ frequency. The upshift is (13 ± 3) cm⁻¹ in C₆₀(AsF₆)_x and (14 ± 3) cm⁻¹ in C₆₀(SbF₆)_x.

In the theory of Jishi and Dresselhaus [18], the σ-bonding energy from sp² hybrid orbitals is determined for the tangential mode with A_g symmetry. When the atomic orbitals are approximated by Slater orbitals, the atomic potential seen by electrons in the sp² orbitals is altered by the change in screening of the nuclear charge due to the charge transferred from or to the C₆₀. In our case, charge is expected to be transferred from C₆₀ to the negative ion. As a result, the atomic potential will be increased from the reduced screening of the nuclear

charge. There is then a bond length decrease and an increase of the bond-stretching force constant.

This is a simple model which does not use the two bond distances of C_{60} . Also, it does not include the polarons in doped C_{60} . Friedman uses a model of conducting polymers to calculate the polaron state with the addition of electrons to C_{60} [20]. Harigaya [21] employed a similar model to determine the polaron excitations for both electron and hole doping. Dimerization results in accumulation of charge along an equatorial line of the molecule and seven different bond lengths. Thus, there are many changes from doping which cannot be included in the theory of Jishi and Dresselhaus. However the bond lengths shorten with hole doping and the change in bond length in the theory of Jishi and Dresselhaus can be considered to be the mean change.

The calculation by Jishi and Dresselhaus yields a stretching force constant of

$$K = K_0 + 16.7 f_c \quad (2)$$

where f_c is the charge transfer per carbon atom and K_0 is the bond stretching force constant of the undoped C_{60} . It is taken to be $30.5 \text{ eV } \text{\AA}^{-2}$ to yield the frequency of the high-frequency A_g mode in C_{60} . The frequency of the bond-stretching mode is

$$\omega = a\sqrt{K} \quad (3)$$

where a is a constant.

From equation (3), the change in frequency from the frequency ω_0 of the neutral C_{60} is

$$\frac{\omega - \omega_0}{\omega_0} = \frac{1}{2} \left(\frac{K - K_0}{K_0} \right). \quad (4)$$

Then, from equation (2) and the value of K_0

$$\frac{\omega - \omega_0}{\omega_0} = 0.27 f_c. \quad (5)$$

When the measured upshift of 13 cm^{-1} is used in equation (5), it is found that $f_c = 0.033$. However, since there are 60 carbon atoms in C_{60} , the total decrease in charge per C_{60} molecule is two electrons. This charge is transferred to the negative ions and satisfies the charge balance for $C_{60}(\text{AsF}_6)_2$. A fully reacted compound was found to be $C_{60}(\text{AsF}_6)_{1.9}$ [6]. Thus, to within experimental uncertainty, the charge balance of the compound is explained by the oxidation of C_{60} .

These results may be compared to those of $C_{60}X_6$ where X represents an alkali metal such as K, Rb or Cs [17]. The charge transfer is from the alkali metal atoms to the C_{60} and increases the electron shielding. There is a lowering of the high-frequency A_g mode by 40 cm^{-1} . This is from a charge transfer $f_c = 0.1$. Thus, the shift of the transverse A_g mode is explained in C_{60} doped with either the alkali metals or the hexafluorides.

The low-frequency Raman A_g mode is mostly radial in character and the low-frequency H_g Raman-active modes have mixed radial and tangential character. In these modes, the frequency shift from the change in shielding is balanced or overwhelmed by a shift from the electrostatic effects of a non-uniform charge distribution over the C_{60} spheres as explained by Jishi and Dresselhaus. Thus, these Raman-active modes cannot be used to determine the charge transfer in the hexafluoride compounds. The amplitude of the Raman scattering was also not sufficient to determine these frequencies with sufficient accuracy for the determination of the frequency shifts.

The spectrum of $C_{60}(\text{AsF}_6)_x$ in figure 1 provides additional insight. The lines at 527 and 576 cm^{-1} have the frequencies of two of the T_{1u} modes of C_{60} . The absorption of 703 cm^{-1} and 410 cm^{-1} is from the ν_3 and ν_4 vibrations of the AsF_6^- ion since they are the same as

those observed by Begun and Rutenberg [22] from AsF₆⁻. This is direct evidence of the AsF₆⁻ ion in the doped fullerene. The absorption lines at 612, 772 and 785 cm⁻¹, which have not been explained previously, could result from vibrations of the C₆₀ molecule. Only four of the 46 fundamental frequencies of C₆₀ are infrared active from symmetry. However, a strong bond between the dopant and the fullerene may break the symmetry and allow additional frequencies to be infrared active. The vibration modes of C₆₀ have been determined in a force-constant model [23]. Some of the frequencies of the H_u mode are similar to the 612, 772 and 785 cm⁻¹ of C₆₀(AsF₆)_x and may explain them. Next, the broad line centred at 1075 cm⁻¹ in the C₆₀(AsF₆)_x spectrum is attributed to the C–F coupling because it is in the frequency range of the C–F band of monofluoride compounds [19]. This is further evidence of the interaction between C₆₀ and the AsF₆⁻ ion. The C₆₀ infrared mode at 1184 cm⁻¹ is observed in figure 1.

The absorption at 1322, 1410 and 1545 cm⁻¹ was observed previously [9] at 1321, 1405 and 1548 cm⁻¹. This is considered excellent agreement because differences can arise from different doping levels and the width of the absorption. The centre line at 1410 cm⁻¹ shifts to 1428 cm⁻¹ while the other two decrease in amplitude as the AsF₆⁻ is taken out of the sample. The lines at 1321 and 1548 cm⁻¹ are assigned to the H_u frequencies 1385 and 1552 cm⁻¹ calculated from the force constant model [23] and made observable by the change in symmetry from the interaction of the dopant and the C₆₀.

The infrared spectra of K_xC₆₀ and Rb_xC₆₀ observed by Martin *et al* [24] show discontinuous changes from the four distinct phases for 0 ≤ x ≤ 6. Many features are explained by the charge-phonon theory of Rice and Choi [25], in particular, the increase in amplitude and the softening of the 1428 cm⁻¹ mode. In any one phase there is very little change of frequency C₆₀(AsF₆)_x exists in only one phase and can be compared to one phase of the alkali metal compounds. The 1428 cm⁻¹ line softens to 1410 cm⁻¹ at x = 2 and the frequencies of the other lines do not change significantly, which is consistent with the observations of one phase of the alkali metal compounds. Also, there is no enhancement of amplitude which is predicted by the charge-phonon theory, and so it is unlikely that this theory is applicable.

5. Conclusions

C₆₀(AsF₆)_x is formed from the reaction of C₆₀ and AsF₅ gas in liquid SO₂. C₆₀(SbF₆)_x is obtained from the reaction of powders of C₆₀ and NO₂SbF₆ in liquid SO₂. The negative ions AsF₆⁻ and SbF₆⁻ are detected in the far-infrared spectra. The negative charge on the ions comes from the C₆₀ molecule. This is shown by an upshift of (13 ± 3) cm⁻¹ in the tangential A_g Raman mode frequency. This upshift results from a charge decrease of 0.033 electrons per carbon atom. The change in charge of C₆₀ is two electrons. The C₆₀ oxidation is the source of the negative charge of the ions. X-ray diffraction show that there is an ordered arrangement of the molecules. Finally, FIR spectra show the change in the compounds due to air exposure. FIR absorption from C–F coupling and the interaction of AsF₆⁻ with C₆₀ are also indicated.

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