

## Emission FTIR Study of C<sub>60</sub> Thermal Stability and Oxidation

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The all-carbon spherical molecule buckminsterfullerene (C<sub>60</sub>) identified by Kroto et al.<sup>1</sup> has recently been intensively studied.<sup>2-16</sup> This unusual structure is expected to produce unique properties for this molecule and its derivatives. Some studies have already demonstrated its low-temperature superconductivity,<sup>17</sup> magnetic properties,<sup>18</sup> and high molecular mobility.<sup>19</sup> Interest in the vibrational spectroscopy of this molecule has led to theoretical predictions of the infrared and Raman spectra<sup>4-11</sup> and the use of infrared spectroscopy to identify, characterize, and confirm its icosahedral structure. The IR emission spectrum of gas-phase buckminsterfullerene has been published,<sup>16</sup> and it was shown that the molecule is apparently stable up to 950 °C under low pressure inert gas conditions. Recently, Milliken et al.<sup>20</sup> used TGA to investigate the thermal stability and oxidation of C<sub>60</sub>. These workers showed that C<sub>60</sub> begins to lose weight in air at ~480 °C, with complete weight loss at ~650 °C. Unfortunately this technique could not be used to study the structural changes occurring during their oxidation. Here we present solid-state emission spectra up to 650 °C and use this technique to study oxidation of the molecule. The C<sub>60</sub> was prepared using the carbon arc technique of Hauffler et al.<sup>2</sup> and purified by chromatography on alumina with hexane solvent.<sup>15</sup>

The C<sub>60</sub> molecule has four main IR bands<sup>3</sup> at 1429, 1183, 577, and 528 cm<sup>-1</sup>, assigned to the F<sub>1u</sub> vibrational mode.<sup>14</sup> The emission

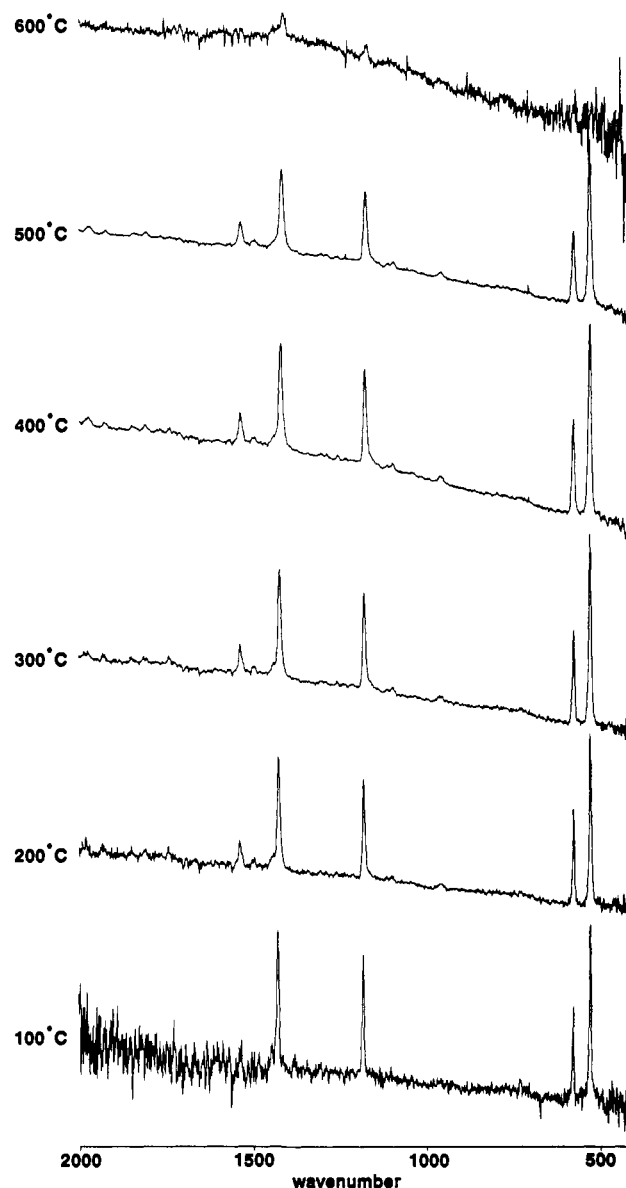


Figure 1. Infrared emission spectra of C<sub>60</sub> obtained at the temperatures indicated. The spectra were obtained on a modified Digilab FTS-7 spectrometer using a newly developed high-temperature emission cell.<sup>26,27</sup> Spectra at a resolution of 2 cm<sup>-1</sup> were acquired by obtaining the ratio of the single beam spectrum of the sample (~100 μg) at temperature to the single beam spectrum of a polished platinum support (background) at the same temperature. The ordinate is percent emission relative to the platinum background. Sixty-four scans were accumulated at each temperature. The platinum reaction surface may catalyze the oxidation, although identical experiments with graphite did not reveal any obvious signs of oxidation until temperatures above 550 °C.

spectra obtained at temperatures between 100 and 650 °C, shown in Figure 1, closely resemble published transmission spectra. The weak band at 1537 cm<sup>-1</sup> is as yet unassigned. Clearly there is very little change in the spectrum as the temperature is increased to 550 °C, except for a shift to lower frequency of all the bands. The observation of an IR frequency shift with increasing temperature is consistent with studies on ionic crystals<sup>21</sup> in which thermal expansion and anharmonicity generally result in a decrease in the band frequency ( $\nu$ ), but few high-temperature data are available for molecular crystals. This frequency change ( $\delta\nu$ ) for temperature change  $\delta t$ (°C) for C<sub>60</sub> can be described by

$$\delta\nu = \delta t(2.64 \times 10^{-5}\nu - 7.35 \times 10^{-3}) \quad r^2 = 0.934$$

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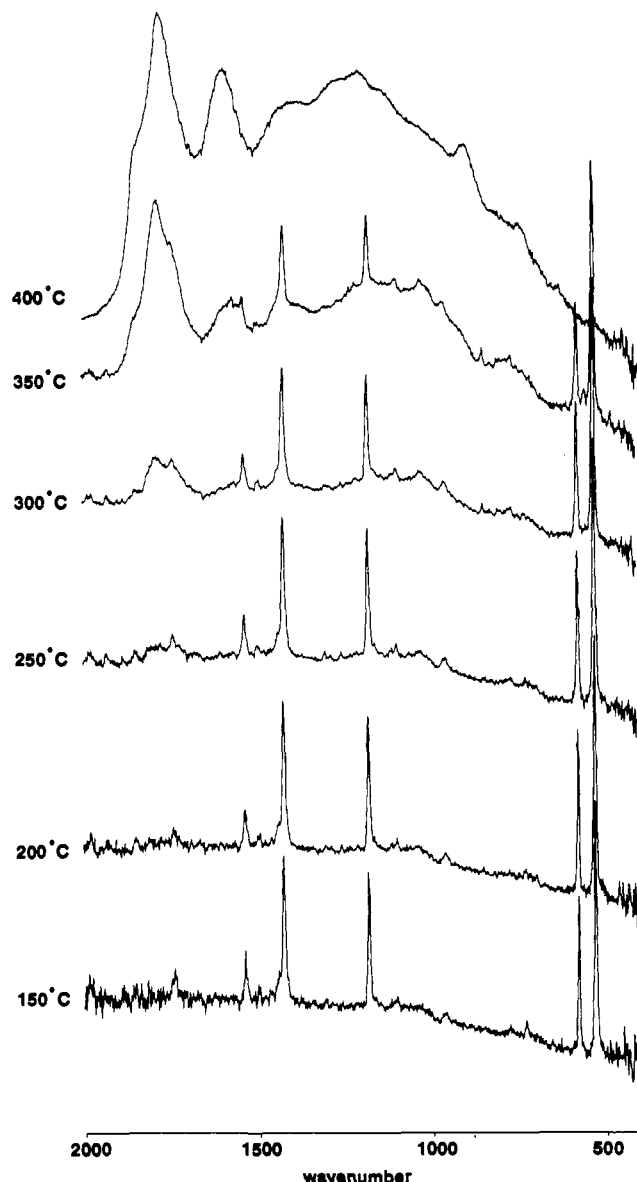


Figure 2. Infrared emission spectra of  $C_{60}$  obtained under  $O_2/Ar$  (25% v/v) using conditions similar to those described in Figure 1.

At 600 °C, however, the signal intensity has decreased dramatically, indicating that the sample has substantially sublimed between 550 and 600 °C. Although subjected to no more than 60 s at each temperature, and a similar time period between each temperature hold point, it is evident that  $C_{60}$  is thermally stable within this temperature range.

Oxidation experiments were carried out by introducing a mixture of oxygen in argon (25% v/v) into the sample chamber. The spectra obtained under this atmosphere are shown in Figure 2. There is no noticeable change in the spectra obtained at 100 and 150 °C, but the spectrum at 200 °C displays small additional broad emission peaks at 1743, 1102, 1037, and 958  $cm^{-1}$ . Upon further heating to 250 °C, these bands increase in intensity up to 300 °C, when a strong broad band appears at 1786  $cm^{-1}$ , in addition to the other bands. By 350 °C this band has developed a shoulder at 1844 and 1735  $cm^{-1}$  and another broad band centered at ~1590  $cm^{-1}$  has developed. More bands are also evident at 2323 ( $CO_2$ ) and 2128  $cm^{-1}$  (CO). A broad emission band has also formed between 700 and 1500  $cm^{-1}$ . Above 350 °C the 1416- and 1174- $cm^{-1}$  bands of  $C_{60}$  are no longer clear although the two low-frequency peaks are still present at lower intensity. All evidence of  $C_{60}$  has gone by 450 °C, and no signal from any species is seen above 550 °C (not shown). Similar experiments carried out at a constant temperature of 250 °C reveal that the emission bands of  $C_{60}$  decrease steadily with time until approximately 90

min, after which no evidence of the  $C_{60}$  molecule can be detected. The apparent discrepancy between the results obtained by Milliken et al.<sup>20</sup> and the results presented here are easily resolved. Milliken et al.<sup>20</sup> have used weight loss as an indicator of reactivity. It is clear from our results that oxidation is occurring at lower temperatures, however, our results also show, in agreement with Milliken et al.,<sup>20</sup> that by 500 °C a large fraction of the sample has oxidized to gas-phase products.

The destruction of the icosahedral symmetry by the addition of oxygen renders the IR spectrum much more complex; nevertheless, some interpretation is possible. The assignment of the strong band at 1780  $cm^{-1}$  in the spectrum obtained at 350 °C is consistent with five-membered-ring lactones, but their formation in the absence of hydroxy groups would not be facile. Vibrational bands in the 1850–1750- $cm^{-1}$  region of oxidized carbons and chars can, however, usually be assigned to cyclic anhydrides,<sup>22,23</sup> e.g., phthalic anhydride, and the ~60- $cm^{-1}$  band separation (between 1844 and 1786  $cm^{-1}$ ) is typical of five-membered rings, although the presence of six-membered cyclic anhydrides condensed to aromatic systems is also a possibility. The main emission band centered at ~1600  $cm^{-1}$  in the spectra obtained at 400 °C and above is very similar to that observed in coal and heat-treated carbonaceous material and has been assigned to an aromatic C–C stretch enhanced by polar functional groups.<sup>24,25</sup>

Although the mechanism of oxygen addition is as yet undetermined, it is clear that a complex product is the result and that anhydrides may be implicated in this mechanism.

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### Polymeric Polyhalogenated Metalloporphyrin Catalysts for Hydroxylation of Alkanes and Epoxidation of Alkenes

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The development of electronegatively substituted heme catalysts<sup>1–6</sup> has provided rapid, high-yield, high-turnover oxidations

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