

# Saturated Vapor Pressure and Sublimation Enthalpy of Fluorine Derivatives of C<sub>60</sub>

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Knudsen cell mass spectrometry and Knudsen effusion method were used to determine the saturated vapor pressures of fluorine derivatives C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub> in the temperature intervals 408–539 K and 395–528 K, respectively; the recommended values are described by the temperature equations:  $\ln(p\{\text{C}_{60}\text{F}_{36}\}/\text{Pa}) = (-16292 \pm 939)/(T/\text{K}) + (30.90 \pm 1.97)$  and  $\ln(p\{\text{C}_{60}\text{F}_{48}\}/\text{Pa}) = (-13146 \pm 827)/(T/\text{K}) + (24.34 \pm 1.71)$ . The sublimation enthalpies were also determined:  $\Delta_{\text{sub}}H_{466}^{\circ}\{\text{C}_{60}\text{F}_{36}\} = (135 \pm 8) \text{ kJ/mol}$  and  $\Delta_{\text{sub}}H_{476}^{\circ}\{\text{C}_{60}\text{F}_{48}\} = (109 \pm 7) \text{ kJ/mol}$ . Ancillary experiments demonstrated that C<sub>60</sub>F<sub>48</sub> vaporizes without decomposition.

## 1. Introduction

Fluorinated fullerenes were among the first derivatives obtained soon after a method of macroscopic preparation of C<sub>60</sub> was invented.<sup>1</sup> Addition of as many as 30–50 fluorine atoms was observed in reactions with F<sub>2</sub> and KrF<sub>2</sub>.<sup>2–4</sup> Such derivation has led to drastic changes in properties in comparison with the pristine fullerene. Of particular interest are the remarkable fluorinating and oxidizing ability,<sup>5</sup> facile solubility in polar solvents, and relatively high thermal stability. The latter allows one to apply mass spectrometry for analysis of fluorofullerenes.<sup>6</sup> By contrast, other halogenated fullerenes (chloro- and bromo-derivatives) degrade under thermal desorption/ionization conditions<sup>7</sup> and cannot be transported via the gas phase. Although fluorofullerenes were reported to sublime without degradation,<sup>8</sup> data on their saturated vapor pressure have not been reported to date because of the difficulty in obtaining compounds with a specific number of fluorine atoms. Recently, progress in the synthesis of specific fluorofullerenes C<sub>60</sub>F<sub>36</sub><sup>9</sup> and C<sub>60</sub>F<sub>48</sub>,<sup>10</sup> which were characterized as individual products, has been made. Preliminary results on the sublimation of C<sub>60</sub>F<sub>36</sub><sup>11,12</sup> have already been published.

Here we report on our further investigation into the thermodynamic properties of fluorofullerenes and present measurements of the saturated vapor pressure of C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub>.

## 2. Experimental Section

**2.1. Sample Preparation.** C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub> were obtained by the interaction of C<sub>60</sub> with MnF<sub>3</sub> and F<sub>2</sub>, respectively, using the synthetic procedures reported earlier.<sup>9,10</sup> Chemical analysis of these samples showed the compositions to be C<sub>60</sub>F<sub>36±1</sub> and C<sub>60</sub>F<sub>48±1</sub>, respectively. The C<sub>60</sub>F<sub>36</sub> sample was repeatedly washed with *n*-hexane to remove oxyfluoride impurities (C<sub>60</sub>F<sub>34</sub>O, C<sub>60</sub>F<sub>36</sub>O). The oxyfluorides were separated because of their better solubility in *n*-hexane in comparison with fluoride C<sub>60</sub>F<sub>36</sub>. As a result the content of oxyfluorides decreased by a factor of 3–5, according to mass spectrometric analysis. In the mass spectrum of C<sub>60</sub>F<sub>36</sub>, in the mass range 1360–1445 amu, the following ions were present: C<sub>60</sub>F<sub>38</sub><sup>+</sup> (14%), C<sub>59</sub>F<sub>35</sub><sup>+</sup> (2%), C<sub>60</sub>F<sub>36</sub>O<sup>+</sup> (2%), C<sub>60</sub>F<sub>36</sub><sup>+</sup> (100%), C<sub>59</sub>F<sub>33</sub><sup>+</sup> (23%), C<sub>60</sub>F<sub>34</sub>O<sup>+</sup>

(4%), and C<sub>60</sub>F<sub>34</sub><sup>+</sup> (2%); of these, C<sub>60</sub>F<sub>38</sub><sup>+</sup>, C<sub>60</sub>F<sub>36</sub>O<sup>+</sup>, C<sub>60</sub>F<sub>36</sub><sup>+</sup>, C<sub>60</sub>F<sub>34</sub>O<sup>+</sup>, are molecular ions whereas C<sub>59</sub>F<sub>35</sub><sup>+</sup> and C<sub>59</sub>F<sub>33</sub><sup>+</sup> are fragments from the C<sub>60</sub>F<sub>38</sub> and C<sub>60</sub>F<sub>36</sub> molecules, respectively.<sup>11</sup> While further purification of C<sub>60</sub>F<sub>38</sub> can be, in principle, achieved by chromatography<sup>13</sup> it is still not possible to prepare the macroscopic quantities of material needed for the experiment described here. The sample of C<sub>60</sub>F<sub>48</sub> was used as prepared.

**2.2. Vapor Pressure Measurements. Two Independent Experimental Techniques.** The Knudsen cell mass spectrometry (KCMS) and the Knudsen effusion-weight loss (KEM) were used in our thermodynamic study.

**Knudsen Cell Mass Spectrometry (KCMS).** A magnetic sector MI-1201 (Russia) mass spectrometer combined with a Knudsen cell assembly was employed; details of the method and instrumentation are described elsewhere.<sup>14</sup> The effusion cell was resistively heated and its temperature was measured by a calibrated Pt/Pt–Rh thermocouple. The molecular beam effusing from the cell was ionized with 70 eV electrons.

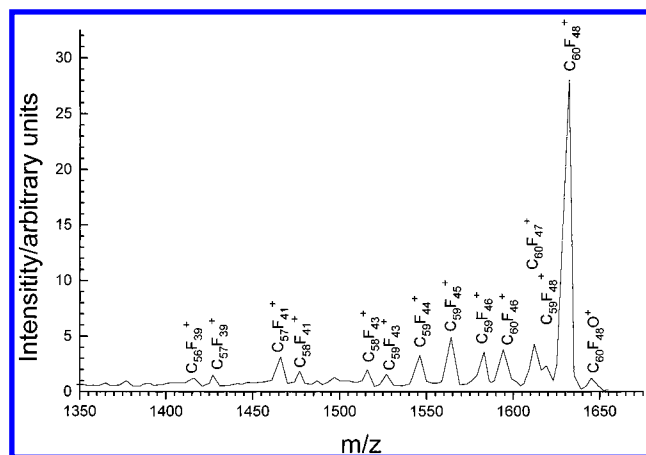
The saturated vapor pressure within the cell is related to the ion current by eqs 1a and 1b:

$$p_j = kI_{ij}T/\sigma_{ij} \quad (1a)$$

$$p_j = kI_jT/\sigma_j \quad (1b)$$

where  $p_j$  is the vapor pressure;  $I_{ij}$ , current of the  $i$ th ion from molecule  $j$ ;  $I_j$ , total ion current from the  $j$ th molecule,  $T$ , absolute temperature;  $\sigma_{ij}$ , partial ionization cross section of formation of the  $i$ th ion from the  $j$ th molecule;  $\sigma_j$ , total ionization cross section of the  $j$ th molecule; and  $k$ , sensitivity coefficient of the instrument.

The calibration of the instrument was accomplished by two methods: (a) measurement of the ion intensity of a standard substance whose vapor pressure at the temperature of the measurement is well-known (in our case PbI<sub>2</sub>)<sup>15</sup> and (b) quantitative isothermal evaporation of a known amount of sample under study.<sup>14</sup> In the first method of calibration (a) the following procedure was employed. We measured the total ion current from the molecule PbI<sub>2</sub> at 505, 516, 539, and 561 K; the saturated vapor pressure values at these temperatures from



**Figure 1.** Electron ionization mass spectrum of studied C<sub>60</sub>F<sub>48</sub> sample at 558 K. Mass range 1350–1650 amu.

the literature<sup>15</sup> are  $1.037 \times 10^{-3}$ ,  $2.337 \times 10^{-3}$ ,  $1.156 \times 10^{-2}$ , and  $4.701 \times 10^{-2}$  Pa, respectively. Therefore, through eq 1b the  $k/\sigma_j$  value for each measurement could be calculated. These  $k/\sigma_j$  values were averaged and used to find the vapor pressure of C<sub>60</sub>F<sub>36</sub>. To this end, the ionization cross section ratio  $\sigma\{\text{C}_{60}\text{F}_{36}\}/\sigma\{\text{PbI}_2\}$  was estimated by the additivity rule.<sup>16</sup> In the second method of calibration (b), we evaporated a known amount of C<sub>60</sub>F<sub>36</sub> measuring the time and evaluated  $k/\sigma_j$  for C<sub>60</sub>F<sub>36</sub> according to the procedure described elsewhere.<sup>14</sup> A Pt twin effusion cell with effusion holes 0.5 mm in diameter was used in both sets of experiments. The evaporation/effusion surface area ratio was estimated to be nearly 400. To check the symmetry of the beams effusing from the two separate chambers of the cell, C<sub>60</sub> was vaporized simultaneously from the two chambers and the measured C<sub>60</sub><sup>+</sup> ion currents were found to be equal within the accuracy of the method (a few percent). In the case of calibration with method (a), a sample of the fluorofullerene under study (ca. 10 mg) and the standard (PbI<sub>2</sub>) were placed into separate chambers of the cell. To derive the saturated vapor pressure, C<sub>60</sub>F<sub>36</sub><sup>+</sup> and C<sub>60</sub>F<sub>48</sub><sup>+</sup> ion currents and the ion currents generated from ionization of PbI<sub>2</sub> were measured at different temperatures. In the calibration experiment (b), weighed samples of C<sub>60</sub>F<sub>36</sub> (10 mg) and C<sub>60</sub>F<sub>48</sub> (10 mg) were also loaded into the separate chambers and allowed to evaporate completely. The dependence of C<sub>60</sub>F<sub>36</sub><sup>+</sup> (from the first chamber) and C<sub>60</sub>F<sub>48</sub><sup>+</sup> (from the second chamber) ion currents on time was recorded at two temperatures, 481 and 528 K.

The mass spectrum of the C<sub>60</sub>F<sub>48</sub> sample in the mass range 1350–1650 amu is shown in Figure 1. In addition to the peaks in the high mass range an intense peak corresponding to CF<sub>3</sub><sup>+</sup>, with intensity of the same order as that of C<sub>60</sub>F<sub>48</sub><sup>+</sup>, was also observed in the low mass region of the spectrum. Its origin and ionization features will be discussed later. The observation of CF<sub>3</sub><sup>+</sup> and other ion series C<sub>n</sub>F<sub>2n+1</sub><sup>+</sup> with  $n = 1-4$  and C<sub>n</sub>F<sub>2n-1</sub><sup>+</sup> with  $n = 3-5$  was first reported in an ionization and fragmentation dynamics study of highly fluorinated fullerenes by single photon absorption.<sup>17</sup>

In this study independent experiments aimed at the determination of the ionization energies of C<sub>60</sub>F<sub>48</sub><sup>+</sup> and CF<sub>3</sub><sup>+</sup> by means of a Nuclide-Patco 90HT magnetic sector mass spectrometer equipped with a Knudsen cell assembly were carried out. In this case the single effusion cell was made of nickel and had an effusion orifice 1 mm in diameter.

**Knudsen Effusion Method (KEM).** In the Knudsen effusion-weight loss experiments a Setaram B60 vacuum thermobalance was used. C<sub>60</sub>F<sub>36</sub> or C<sub>60</sub>F<sub>48</sub> (ca. 20 mg) was placed into a nickel effusion cell. To determine the saturated vapor pressure, the

**TABLE 1: Saturated Vapor Pressure over C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub> Measured by KEM**

C <sub>60</sub> F <sub>36</sub>		C <sub>60</sub> F <sub>48</sub>	
T/K	P/Pa	T/K	P/Pa
478	0.0428	473	0.0317
486	0.0819	475	0.0380
496	0.134	486	0.0690
503	0.216	494	0.108
505	0.253	498	0.110
512	0.531	502	0.156
514	0.393	504	0.181
516	0.483	506	0.181
520	0.534	515	0.289
521	0.891	516	0.365
528	0.714	527	0.535
530	1.42		

mass loss rate was measured at various temperatures. The vapor pressure is related to the mass loss rate by the well-known relation:

$$p = (dm/dt)K^0(T/M)^{1/2} \quad (2)$$

where  $(dm/dt)$  is the mass loss rate;  $M$ , molar mass; and  $K^0$ , instrumental constant. The instrumental constant, which depends on the size of the effusion orifice, and its Clausing factor,<sup>14</sup> was determined by vaporizing pure cadmium.

Finally, to check the average molecular weight of the effusing vapor over C<sub>60</sub>F<sub>48</sub> independent measurements were made at different temperatures using the combined torsion effusion – thermobalance technique. Indeed, the torsion-effusion method provides a measure of the absolute pressure, while, by the simultaneous measurement of the weight loss rate of the sample,  $dm/dt$ , with the thermobalance one can evaluate through eq 2 the average molecular weight of the effusing species.

### 3. Results and Discussion

**C<sub>60</sub>F<sub>36</sub>.** The saturated vapor pressure of C<sub>60</sub>F<sub>36</sub> determined by KEM experiments in the temperature range 478–530 K are reported in Table 1. The contribution to the vapor pressure of the possible residual impurities (C<sub>60</sub>F<sub>38</sub>, C<sub>60</sub>F<sub>36</sub>O, and C<sub>60</sub>F<sub>34</sub>O) was neglected. Indeed the influence on the total vapor pressure of this type of residual impurities has been shown<sup>11</sup> to be minor. It should also be noted that, according to eq 2, the influence of a small difference in the molecular weight on the vapor pressure is negligible. In the preliminary results<sup>12</sup> reported earlier two nickel crucibles of different size were employed in the two set of measurements performed. Later checks showed that only in the case of one of these crucibles, that of smaller size, was the attainment of true equilibrium within the cell itself fully realized. Even though the absolute values of the pressure in the two series of measurements were in good agreement, we prefer to retain the results of only one of the aforementioned series because of the greater reliability of its  $\ln P$  vs  $1/T$  dependence.

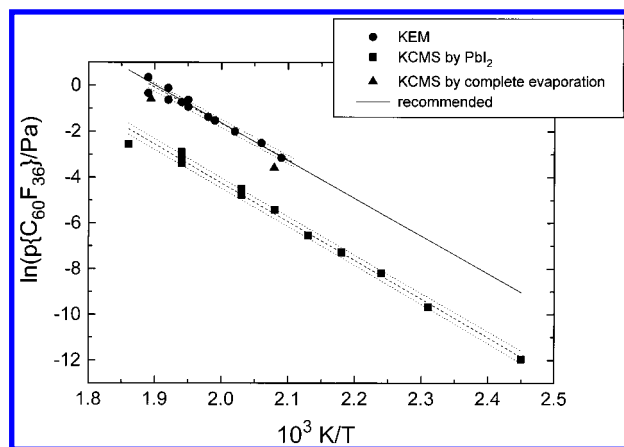
In the KCMS experiment, the vapor pressure values for C<sub>60</sub>F<sub>36</sub> derived using the aforementioned calibration procedure (b) at two temperatures were the following:

$$p\{\text{C}_{60}\text{F}_{36}, 481 \text{ K}\} = 0.028 \text{ Pa and}$$

$$p\{\text{C}_{60}\text{F}_{36}, 528 \text{ K}\} = 0.56 \text{ Pa}$$

which agree satisfactorily with the KEM data (see also Figure 2).

To derive the vapor pressure in KCMS experiments using calibration procedure (a), the vapor pressure data for the PbI<sub>2</sub> standard were taken from the reference literature,<sup>15</sup> the total



**Figure 2.** The plot of  $\ln(p\{C_{60}F_{36}\}/Pa)$  versus  $1/T$  obtained by the different methods (see legend) and the recommended temperature equation line. Regression lines (dashed) and confidence bands (dot) obtained by least-squares fitting treatment are also presented.

ionization cross sections for  $C_{60}F_{36}$  and  $PbI_2$  were estimated using the additivity rule,<sup>16</sup> and the multiplier gain was assumed equal for the two species. Indeed the electron multiplier gain of our apparatus has been measured in other experiments to be nearly the same for the  $PbI_2$  and the simple fullerenes thus suggesting that it does not depend on the mass in this range. The temperature dependence of the vapor pressure hence derived is described by the following equation in the temperature interval 408–539 K:

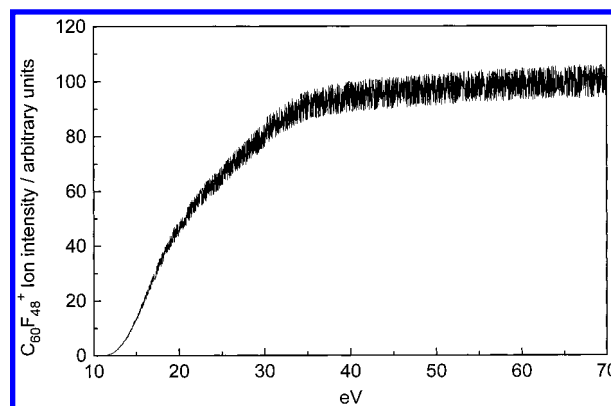
$$\ln(p\{C_{60}F_{36}\}/Pa) = (-16745 \pm 1055)/(T/K) + (29.21 \pm 2.20) \quad (3)$$

and plotted in Figure 2. In eq 3 and throughout this work, uncertainties are quoted at the 95% confidence limits. Clearly the vapor pressure values are significantly lower than those obtained from the KEM measurements and also from the KCMS experiment using procedure (b) (see Figure 2). We believe that such discrepancies originate from the failure of the additivity rule in the estimate of the total ionization cross section ratio for molecules that differ considerably in size and structure. Actually, to attain the agreement between the KCMS pressures evaluated by the two methods one should adopt a cross section ratio  $\sigma\{C_{60}F_{36}\}/\sigma\{PbI_2\} = 1.18$  rather than 7.14 as estimated by the additivity rule.

To select a recommended value for the sublimation enthalpy we considered the three values of the sublimation now available for  $\Delta_{sub}H^\circ\{C_{60}F_{36}\}$ : a first value,  $(134 \pm 6)$  kJ/mol determined earlier,<sup>11,12</sup> and the two values determined here, namely,  $(132 \pm 18)$  kJ/mol derived from least-squares fitting of the KEM results and  $(139 \pm 9)$  kJ/mol from the slope of the KCMS eq 3. It is worth noting here that the sublimation enthalpy derived above from the slope does not depend on the procedure adopted for the determination of the ionization cross sections. The above values were averaged with the weights inversely related to their dispersions, thus yielding the recommended value:  $\Delta_{sub}H^\circ\{C_{60}F_{36}\} = (135 \pm 8)$  kJ/mol

The recommended temperature dependence of the saturated vapor pressure of  $C_{60}F_{36}$  in the temperature interval 408–539 K was obtained using the above sublimation enthalpy value  $(135 \pm 8)$  kJ/mol and the saturated vapor pressure values measured by KEM (see Table 1):

$$\ln(p\{C_{60}F_{36}\}/Pa) = (-16292 \pm 939)/(T/K) + (30.90 \pm 1.97) \quad (4)$$



**Figure 3.** Ionization efficiency curve measured for the ion  $C_{60}F_{48}$ .

The intercept given in this equation is the average of the values calculated for each of the vapor pressure points, measured by the KEM method and reported in Table 1, through the equation  $\ln(p/Pa) = -\Delta_{sub}H^\circ/RT + B$ . The errors given include the uncertainty in the recommended sublimation enthalpy and the experimental error. The latter was calculated as  $t_{0.95,11}\sigma/n^{1/2}$ , where  $t_{0.95,11}$  is Student's coefficient;  $\sigma$ , standard deviation; and  $n$ , number of points.

**$C_{60}F_{48}$ .** The KEM method was used to determine the total vapor pressure over  $C_{60}F_{48}$  in the temperature interval 473–527 K. The results are presented in Table 1.

In the interpretation of the KCMS experiments on  $C_{60}F_{48}$  we faced the problem of the assignment of the intense  $CF_3^+$  peak in the mass spectrum. On one hand, it may be formed from the gaseous products of thermal degradation of  $C_{60}F_{48}$  (most probably  $CF_4$ ). On the other hand, one cannot rule out the possibility of formation of the low mass ion as a result of dissociative ionization of  $C_{60}F_{48}$ , as for example,  $C_{60}F_{48} + e^- \rightarrow C_{59}F_{45} + CF_3^+ + 2e^-$ ,  $C_{60}F_{48} + e^- \rightarrow C_{59}F_{44} + F + CF_3^+ + 2e^-$ , and  $C_{60}F_{48} + e^- \rightarrow C_{59}F_{43} + 2F + CF_3^+ + 2e^-$ . In the case of thermal degradation which may be accompanied by formation of  $CF_4$ , a product with higher carbon content than  $C_{60}F_{48}$  must be formed. This product (or products) would either effuse with  $C_{60}F_{48}$  and thus should be observable in the mass spectrum or remain as unvolatile residue inside the effusion chamber after evaporation. However, neither any related ion in the mass spectrum nor an appreciable residue in the effusion chamber were observed. We assume consequently that the most probable source of  $CF_3^+$  is fragmentation. This agrees with the result of H. Steger et al.<sup>17</sup> who studied the ionization of a  $C_{60}F_{46,48}$  mixture under synchrotron radiation conditions. These authors who first reported on the presence of unusually intense ions in the lower range of the mass spectra of fluorofullerenes, from dissociation experiments on size-selected  $C_{60}F_x^+$  ions, concluded that  $CF_3^+$  and other low mass ion series  $C_nF_{2n+1}^+$  ( $n = 1-4$ ) and  $C_nF_{2n-1}^+$  ( $n = 3-5$ ) were most likely real daughter ions. One more argument in favor of the origin of the  $CF_3^+$  peak as a fragment from  $C_{60}F_{48}$  is the good cutoff of ion current observed by placing a mechanical shutter between the effusion cell and ionization chamber; the cutoff is usually poor in the case of ions originating from permanent gas or highly volatile species.

To substantiate these conclusions under the conditions of our experiments we measured the ionization efficiency curves (IEC) of  $C_{60}F_{48}^+$  and  $CF_3^+$  with the Nuclide-Patco mass spectrometer. With this instrument the ion intensity ratio  $CF_3^+/C_{60}F_{48}^+$  was found 5:1 at 70 eV. The IEC of the fluorofullerene  $C_{60}F_{48}$  is reported in Figure 3. The appearance energies (AE) values obtained by the linear extrapolation method and by the vanishing



current method are 13.0 eV (linear extrapolation) and 12.0 eV (vanishing current) for C<sub>60</sub>F<sub>48</sub><sup>+</sup> and 15.0 eV (linear extrapolation) and 13.5 eV (vanishing current) for CF<sub>3</sub><sup>+</sup>, respectively. The AE values of C<sub>60</sub>F<sub>48</sub> determined here by electron ionization is in agreement with the value 12.0 eV measured by photoionization for C<sub>60</sub>-based molecules.<sup>17</sup> Our AE value of 13.5 to 15 eV measured for the CF<sub>3</sub><sup>+</sup> ion rules out its origin from CF<sub>3</sub>(g), the AE of which is quoted as 10.1–10.2 eV.<sup>18</sup> On the other hand, although somewhat lower, it would still be compatible with the dissociative ionisation from CF<sub>4</sub>(g) with an AE (threshold) value reported to be 15.4–16.2 eV (electron impact) and 15.2–15.3 eV (photoionization).<sup>18</sup> We further observe that the break downward at about 20 eV in the C<sub>60</sub>F<sub>48</sub> IEC (see Figure 3) is probably due to the opening of a number of fragmentation channels to all the various ions observed.

These results do not suffice to definitely settle the question of the occurrence of some sample decomposition. Therefore an independent check of the vapor composition over C<sub>60</sub>F<sub>48</sub> has been performed by simultaneous torsion effusion weight-loss measurements at few temperatures within the temperature range considered with the same assembly used in the previous study of pristine fullerenes.<sup>19</sup> The values of the molecular weight measured at three temperatures: 499, 508 and 530 K were 1616, 1660 and 1620 amu, respectively, with an average of 1633 amu, in excellent agreement with the nominal molecular weight of C<sub>60</sub>F<sub>48</sub> (1632). This constitutes a clear-cut proof that C<sub>60</sub>F<sub>48</sub> sublimates without decomposition. Further, the total pressure values measured with the torsion effusion apparatus, namely, 0.10, 0.13, and 0.56 Pa at the temperatures reported above, confirmed the values measured by KEM.

In the KCMS study the saturated vapor pressure of C<sub>60</sub>F<sub>48</sub> was obtained as for C<sub>60</sub>F<sub>36</sub> by two independent methods of calibration. In the first one performed with PbI<sub>2</sub> as standard the result is given by eq 5 in the 395–516 K interval:

$$\ln(p\{\text{C}_{60}\text{F}_{48}\}/\text{Pa}) = (-13349 \pm 836)/(T/\text{K}) + (24.14 \pm 1.90) \quad (5)$$

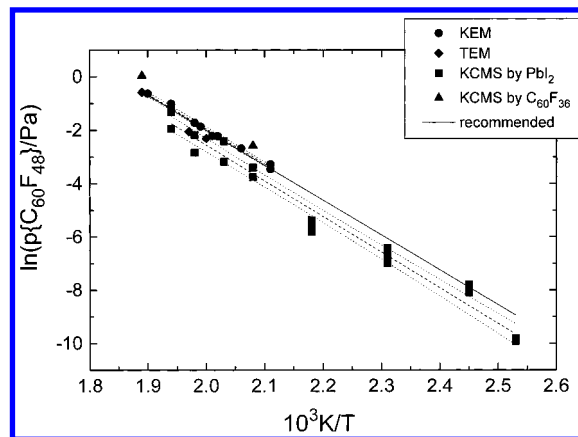
The second method involved direct measurements of the C<sub>60</sub>F<sub>48</sub><sup>+</sup>/C<sub>60</sub>F<sub>36</sub><sup>+</sup> intensities ratio in the experiment in which C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub> were placed into separate chambers of the twin cell. For the vapor pressure calculations we used the saturated vapor pressure values of C<sub>60</sub>F<sub>36</sub> at 481 K and 528 K reported here. The ionization cross section ratio was taken as  $\sigma\{\text{C}_{60}\text{F}_{36}\}/\sigma\{\text{C}_{60}\text{F}_{48}\} = 0.93$  using the additivity rule.<sup>16</sup> The resulting data are  $p\{\text{C}_{60}\text{F}_{48}, 481 \text{ K}\} = 0.076 \text{ Pa}$  and  $p\{\text{C}_{60}\text{F}_{48}, 528 \text{ K}\} = 1.04 \text{ Pa}$ .

As in the case of C<sub>60</sub>F<sub>36</sub>, the comparison of these results (see Figure 4) reveals a smaller but still significant difference between the saturated vapor pressure values obtained with the use of the PbI<sub>2</sub> standard and the data obtained by KEM and in the experiment with direct measurement of C<sub>60</sub>F<sub>48</sub><sup>+</sup>/C<sub>60</sub>F<sub>36</sub><sup>+</sup> ion current ratios. To attain the agreement between the obtained results one should take  $\sigma\{\text{C}_{60}\text{F}_{48}\}/\sigma\{\text{PbI}_2\} = 2.63$  rather than 7.69 as estimated by the additivity rule.

The recommended sublimation enthalpy of C<sub>60</sub>F<sub>48</sub> was obtained by taking into account the value (108 ± 7) kJ/mol derived by the least-squares treatment of the KEM data points in Table 1 and (111 ± 7) kJ/mol calculated from eq 5:

$$\Delta_{\text{sub}}H_{476}^0\{\text{C}_{60}\text{F}_{48}\} = (109 \pm 7) \text{ kJ/mol}$$

The recommended temperature equation of the saturated vapor pressure of C<sub>60</sub>F<sub>48</sub> in the temperature interval 395–528 K was found using the vapor pressure values obtained by KEM (see



**Figure 4.** The plot of  $\ln(p\{\text{C}_{60}\text{F}_{48}\}/\text{Pa})$  versus  $1/T$  obtained by the different methods (see legend) and the recommended temperature equation line. Regression lines (dash) and confidence bands (dot) obtained by least-squares-fitting treatment are also presented.

Table 1) and the above sublimation enthalpy:

$$\ln(p\{\text{C}_{60}\text{F}_{48}\}/\text{Pa}) = (-13146 \pm 827)/(T/\text{K}) + (24.34 \pm 1.71) \quad (6)$$

**Comparison of the Results on C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub>.** Interestingly, the CF<sub>3</sub><sup>+</sup> ion was not observed in the mass spectrum of C<sub>60</sub>F<sub>36</sub> whereas in the mass spectrum of C<sub>60</sub>F<sub>48</sub> it was a dominant peak in the low mass range and comparable with the molecular ion C<sub>60</sub>F<sub>48</sub><sup>+</sup>. This indicates a distinction between their fragmentation channels under electron ionization conditions. This is probably due to the weakening of the C–C bond with the number of fluorine atoms in fluoroderivatives of fullerenes.

The recommended values of the saturated vapor pressure of C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub> are close together in the temperature range investigated. However, the sublimation enthalpy of C<sub>60</sub>F<sub>36</sub>, (135 ± 8) kJ/mol, appears to be greater than that found for C<sub>60</sub>F<sub>48</sub>, (109 ± 7) kJ/mol. This difference indicates that the sublimation enthalpy of fluorine derivatives of fullerene have a tendency to decrease with increasing the fluorine content in a molecule (for comparison the sublimation enthalpy of the parent fullerene:<sup>20</sup>  $\Delta_{\text{sub}}H_{298}^0\{\text{C}_{60}\} = (181 \pm 2) \text{ kJ/mol}$ ). There is also a distinction between the corresponding sublimation entropies calculated from eqs 4 and 6, their values being:

$$\Delta_{\text{sub}}S_{466}^0\{\text{C}_{60}\text{F}_{36}\} = (161 \pm 16) \text{ J/(mol K)}$$

$$\text{and } \Delta_{\text{sub}}S_{476}^0\{\text{C}_{60}\text{F}_{48}\} = (107 \pm 14) \text{ J/(mol K)}$$

In conclusion, we would like to point out that despite the similarity of the C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub> molecules in size and general structural features (both molecules can be roughly represented as spheres with the radius equal to the sum of fullerene cage radius and C–F distance (1.29 Å))<sup>21</sup> a significant difference between them is observed at the molecular level (the difference in fragmentation channels) as well as in the solid (the difference in the sublimation thermodynamic functions).

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## References and Notes

- (1) Huffman, D. R.; Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K. *Nature* **1990**, 347, 354.
- (2) Selig, H.; Lifshitz, C.; Perez, T.; Fisher, J. E.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P.; Smyth, A. B. *J. Am. Chem. Soc.* **1991**, 113, 5475.
- (3) Holloway, J. P.; Hope, E. G.; Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1991**, 966.
- (4) Boltalina, O. V.; Abdul-Sada, A. K.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1995**, 981.
- (5) Gakh, A. A.; Tuinman, A. A.; Adcock, J. L.; Compton, R. N. *Tetrahedron Lett.* **1993**, 34, 7167.
- (6) Tuinman, A. A.; Mukherjee, P.; Adcock, J. L.; Hettich, R. L.; Compton, R. N. *J. Phys. Chem.* **1992**, 96, 7584.
- (7) Birkett, P. R.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. *Nature* **1992**, 357, 479.
- (8) Taylor, R.; Langley, G. J.; Brisdon, A. K.; Holloway, J. H.; Hope, E. G.; Kroto, H. M.; Walton, D. R. *J. Chem. Soc., Chem. Commun.* **1993**, 875.
- (9) Boltalina, O. V.; Borschevskii, A. Ya.; Sidorov, L. N.; Street, J. M.; Taylor, R. *J. Chem. Soc., Chem. Commun.* **1996**, 529.
- (10) Boltalina, O. V.; Sidorov, L. N.; Bagryantsev, V. F.; Seredenko, V. A.; Zapol'skii, A. S.; Street, J. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2275.
- (11) Boltalina, O. V.; Markov, V. Yu.; Borschevskii, A. Ya.; Sidorov, L. N.; Popovich, A. *Mendeleev Commun.* **1996**, 253.
- (12) Boltalina, O. V.; Markov, V. Yu.; Borschevskii, A. Ya.; Galeva, N. A.; Pavlovich, V. K.; Sidorov, L. N.; Gigli, G.; Balducci, G.; Bardi, G. *Mol. Mater.* **1998**, 10, 225.
- (13) Boltalina, O. V.; Street, J. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 649.
- (14) (a) Chilingarov, N. S.; Korobov, M. V.; Sidorov, L. N.; Nit'kin, V. N.; Shipachev, V. A.; Zenskov, S. V. *J. Chem. Thermodynamics* **1984**, 16, 965. (b) Grimley, R. T. In *The Characterization of High-Temperature Vapors*; Margrave, J. L., Ed.; Wiley: New York, 1967; p 195.
- (15) IVTANTHERMO-NIST. Special Database No. 5; CRC Press: Boca Raton, 1993.
- (16) Otvos, J. W.; Stevenson, D. P. *J. Am. Chem. Soc.* **1956**, 78, 536.
- (17) Steger, H.; Mische, U.; Kamke, W.; Ding, A.; Fieber-Erdmann, M.; Drewello, T. *Chem. Phys. Lett.* **1997**, 39, 276.
- (18) Rosenstock, A. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *Energetics of Gaseous Ions*, Suppl.1 to JCPRD; Washington, DC 1977; Vol. 6.
- (19) Brunetti, B.; Gigli, G.; Giglio, E.; Piacente, V.; Scardala, P. *J. Phys. Chem.* **1997**, 101, 10715.
- (20) Piacente, V.; Gigli, G.; Scardala, P.; Giustini, A.; Ferro, D. *J. Phys. Chem.* **1995**, 99, 14052.
- (21) Okino, F.; Kawasaki, S.; Fukushima, Y.; Kimura, M.; Nakajima, T.; Touhara, H. *Fullerene Sci. Technol.* **1996**, 4, 873.