Enthalpy of sublimation of $C_{60}F_{36}$

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The Knudsen cell mass spectrometry method has been applied in order to obtain the enthalpies of sublimation of $C_{60}F_{36}$.

The chemistry of fullerenes is one of the most intensively developing fields in fullerene science. Among the fullerene derivatives fluorinated ones are of special interest because of their high thermal stability and unique oxidizing and fluorinating properties.[1] There have been scarcely any data published on the thermodynamic properties of the fluorofullerenes except for a few studies of the gas phase reactions involving some fluorofullerene molecules[2] and anions of difluorinated fullerenes.[3] So far, no data on thermodynamic functions in the condensed matter phase have been obtained — mainly due to the difficulty of controlling the fluorination process and isolating pure products from the mixture, although the selective synthesis of $C_{60}F_{48}$ has been reported[4] and the preparation of $C_{60}F_{36}$ was recently successfully performed by our group.[5]

We report here the first experimental determination of the enthalpy of sublimation of $C_{60}F_{36}$.

A magnetic sector MI1201 (Russia) mass spectrometer combined with a high temperature ion source was used in our thermodynamic studies.[6] The $C_{60}F_{36}$ sample was prepared by the solid phase reaction of C_{60} with MnF_3 (details are described in our earlier paper[5]). The composition of the sample according to chemical elemental analysis corresponds to C : F = 60 : 36. A weighed amount (5.25 mg) was then placed into the nickel effusion cell. The cell was resistively heated and the temperature was measured with a Pt/PtRh thermocouple. Electrons of energy 70 eV were used to ionize the molecular beam evaporating from the cell.

The electron impact mass spectrum obtained at 425 K is presented in Figure 1. The peaks corresponding to 1420, 1404, 1382, 1366, 1335 and 702 amu were identified in the spectra and they were assigned to the ions $C_{60}F_{36}O^+$, $C_{60}F^+{}_{36}$, $C_{60}F_{34}O^+$, $C_{60}F^+{}_{34}$ and $C_{59}F^+{}_{33}$. The signal at 1404 corresponding to $C_{60}F^+{}_{36}$ was the predominant peak in the available temperature range.

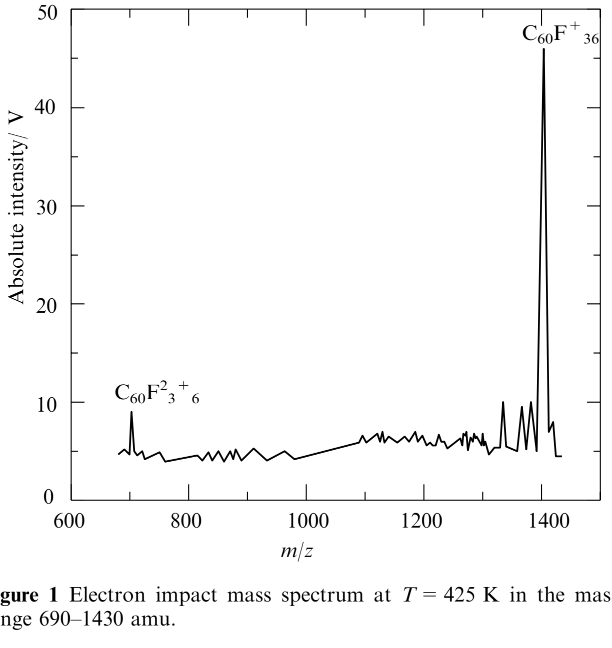

Figure 1 Electron impact mass spectrum at $T = 425$ K in the mass range 690–1430 amu.

To study the molecular presursors of the recorded ions we analysed the mass spectra at different electron energies on a VG double focusing mass spectrometer. Mass spectra obtained at 70 and 12 eV electron energy are shown in Figure 2.

Electron impact ionization is almost unfailingly accompanied by fragmentation of the molecules. One can see from the mass spectra in Figures 2 (*a*) and (*b*) that the intensity corresponding to $C_{59}F^+{}_{33}$ practically vanishes at lower electron energies while $C_{60}F^+{}_{36}$ and $C_{60}F^+{}_{34}$ peaks remain in the spectrum. The CF_3 loss from $C_{60}F_{36}$ gives the most intensive fragment which agrees with earlier collision induced dissociation (CID) experiments performed on highly fluorinated fullerene species.[7] The discrepancy of the ion distributions in the spectra shown in Figures 1 and 2 are most probably due to the interaction of the sample with the glass

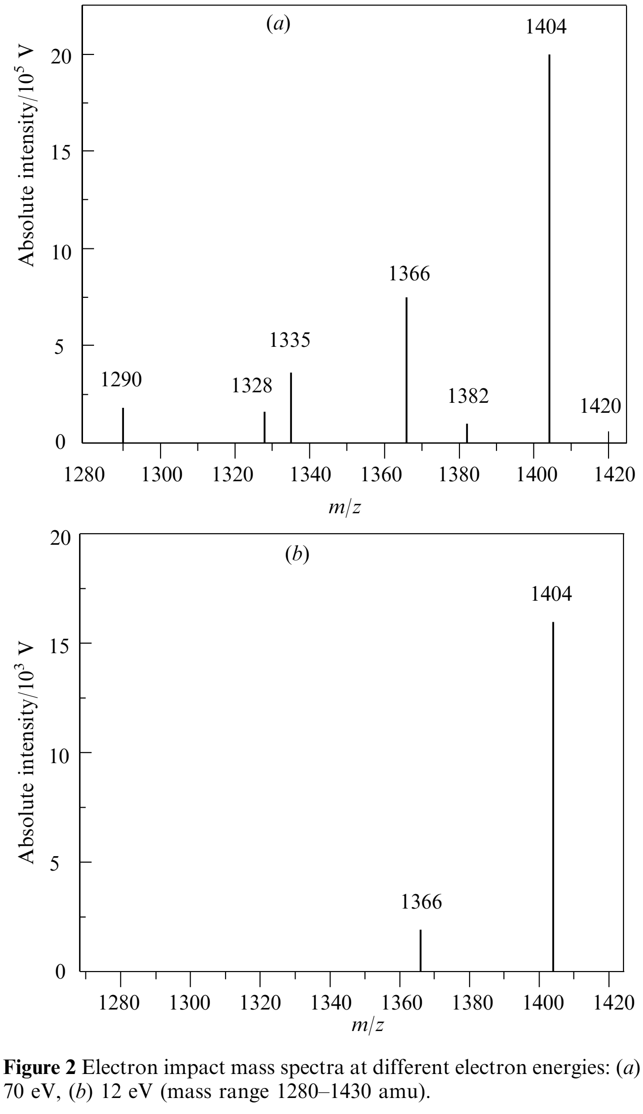

Figure 2 Electron impact mass spectra at different electron energies: (*a*) 70 eV, (*b*) 12 eV (mass range 1280–1430 amu).

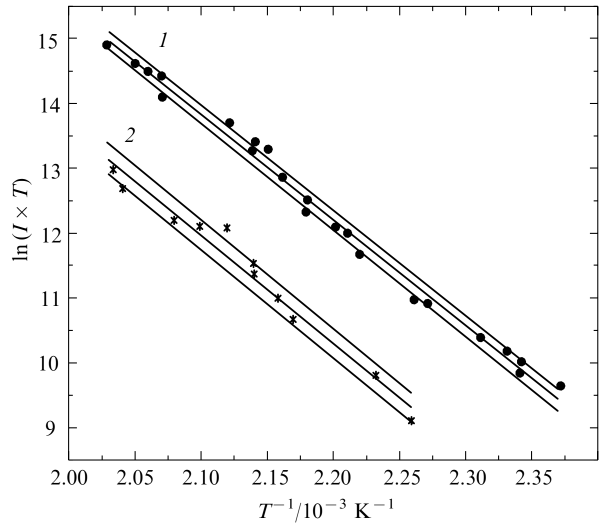

Figure 3 Plot of ln (I × T) *versus* 1/T for $C_{60}F^{+}{}_{36}$ (first series) (*1*) and $C_{60}F_{34}O^{+}$ (*2*). Experimental points, regression lines and confidence bands are presented.

capillary which leads to the partial decomposition of $C_{60}F_{36}$.

Thus small amounts of by-products such as $C_{60}F_{34}$, $C_{60}F_{34}O$ and $C_{60}F_{36}O$ are, apparently, present in the $C_{60}F_{36}$ sample prepared. Attempts to further purify the sample by resublimation or changing the synthesis conditions did not markedly change its composition.[5] High performance liquid chromatography (HPLC) separation may be an alternative way for the future isolation of pure compounds provided one finds the proper solvent and suitable experimental conditions. One can not exclude the possibility of degradation of $C_{60}F_{36}$ under heating or its reaction with the walls of the cell or glass capillary in the mass spectrometer.

Two series of the temperature dependence of $C_{60}F^{+}{}_{36}$ ion were obtained in the temperature range 422–525 K. The enthalpy of sublimation was derived from the equation:

$$\ln(I_{ij}T) = -<\Delta_s H^0_T>_j/RT + C \qquad (1)$$

where I_{ij} is the ion current of an ion i formed from the molecule j; $<\Delta_s H^0_T>$ is the enthalpy of sublimation of compound j (as noted above it is averaged in our case), T is the absolute temperature, R is the universal gas constant, C is a constant depending on the ionization cross-section, sensitivity coefficient and mole fraction in the sample. The enthalpy of sublimation can be calculated from the slope of a plot of $\ln(I_{ij}T)$ *versus* $1/T$.[6]

The slope was derived *via* a least squares treatment of the data. The experimental data obtained for $C_{60}F^{+}{}_{36}$ (one series) and the impurity $C_{60}F_{34}O^{+}$ are plotted in Figure 3 as a function of ln(I × T) *versus* 1/T.

As shown previously in a ^{19}F NMR study[5] the $C_{60}F_{36}$ sample represents a mixture of four isomers and nothing is known of the $C_{60}F_{34}O$ isomers. Therefore the sublimation enthalpy obtained in this work is defined as the value averaged over all the existing isomers:

$$<\Delta_s H^0_T> = \Sigma y_i\,(\Delta_s H^0_T)_i\,, \qquad (2)$$

where y_i is the mole fraction of the i-th isomer and $(\Delta_s H^0_T)_i$ is the enthalpy of sublimation of the i-th isomer. We assume that y_i does not depend on temperature in the available temperature range.

The sublimation enthalpy values obtained for $C_{60}F_{36}$ in two series agree within experimental error and were averaged to further remove uncertainties. The recommended value for the enthalpy of sublimation of $C_{60}F_{36}$ is as follows:

$$<\Delta_s H^0_T\{C_{60}F_{36}\}> = (134\pm6)\ \text{kJ mol}^{-1}$$

We also obtained the partial enthalpy of sublimation of $C_{60}F_{34}O$:

$$\overline{<\mathit{\Delta}_s H^0_T\{C_{60}F_{34}O\}>_m} = (136\pm14)\ \text{kJ mol}^{-1}$$

Assuming the formation of an ideal solution the obtained partial sublimation enthalpy of $C_{60}F_{34}O$ is an estimation of the sublimation enthalpy of this compound.

As pointed out above, nothing has been known to date concerning the evaporation behaviour of fluorofullerenes and no data has been published on the thermodynamic parameters of other fullerene derivatives in the solid phase. Thus it is interesting to compare the obtained data with the sublimation enthalpy of the pristine fullerene C_{60} which is, according to the latest result by Gigli *et al.*,[8] ≈ 50 kJ mol^{-1} higher than that of $C_{60}F_{36}$ [$\Delta_s H^0(C_{60}F_{36}$, 298 K) = (181±2) kJ mol^{-1}].[8]

In summary, the evaporation study of $C_{60}F_{36}$ demonstrated that it is highly thermally stable and that it sublimes congruently without decomposition at lower temperatures than that of pristine C_{60}.

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