

Analysis of Entropic vs. Thermal Fragmentation

B. Dohmen¹, J. Curdes¹, P. Wagner², E. R. Hilf¹, W. Tuszynski¹, K. Wier²,

(1) : Fachbereich Physik, Carl von Ossietzky - Universität, D - 2900 Oldenburg, Germany

(2) : Institut für Kernphysik, TH Darmstadt, D - 6100 Darmstadt, Germany

Abstract

A first *PDMS* spectrum of the highly volatile *decane* is presented and compared to simulation calculations. It is inferred that fragmentation in *PDMS* is mainly entropic with *decane* being specifically hot. In addition we compare calculations on the formation of new compounds from the innermost zone close to the primary ion track.

PDMS – Spectrum of Decane

Spectra of volatile materials such as *decane* have been taken at Darmstadt by *PDMS*. Extreme care has been taken to gain a clean spectrum with no contaminations by sublimating other material from the rest-gas. The fragmentation pattern is typical for positive ion *PDMS* spectra with a relatively high molecular ion peak and a small series of fragments. One of our research lines is the explanation of this *fragmentation process* in *PDMS*.

Entropic Fragmentation in PDMS

The main part of ordinary *PDMS* spectra abundances stems from a large area around the impact ion track. The energy is transferred to the bonds by means of a secondary electron shower in a rather short time as compared to a thermal vibration time. Thus the fragmentation here is thought to be mainly *entropic* which means that probabilities for bond-breaking are almost *independent* from each other because of the high dE/dt , so that there is no time to distribute the enormous amount of energy to other bonds.

A calculation was done using the newly developed code CRUNCHER to simulate the fragmentation pattern by calculating all possible breakup ways of the given chemical structure. We had to assume different probabilities for equal bonds in order to obtain the amplitude pattern observed. This is in contrast to our assumption that the probabilities are independent from each other because of the entropic nature of the process.

The molecular peak of the *PDMS* spectrum is well represented in this way, which is also true for the main fragment lines, but there are fragments around 12 and 108 *amu* which do not appear in the original spectrum. This and the choice of probabilities lead to the assumption that fragmentation of these chain-type molecules has a strong thermal contribution. In other words, that the "temperature" of the gas is quite high compared to other, less chain-like substances where we have obtained results which come more close to our assumptions of *entropic* fragmentation.

Formation of New Compounds from the Central Plasma Zone

Another point of interest is what happens to the material emerging from the track itself, where all matter has been heavily destructed. The resulting atoms or small fragments form a gas which is ejected from the track[2]. It was suspected that in this gas the *formation of new molecules* takes place. What we present here is an example for such a process. The negative ion *PDMS* spectra are believed to be dominated by matter emerging from the ion track. One support for this is the absence of any molecular peak in the negative ion spectra. We identify three different series of Carbon chains in the considered spectra:

- A series of $C_2, C_4, C_6, \dots (24, 48, 72, \dots amu)$
- A series of $C_2H, C_4H, C_6H, \dots (25, 49, 73, \dots amu)$
- A series of $C_3, C_5, C_7, \dots (36, 60, 84, \dots amu)$

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We have studied the relative abundances of these three series for Decane. We compared these with spectra taken from entirely different substances, such as Fullerene and β -Carotene. The similarity of the abundance series of these carbon cluster series is striking. We got strong evidence for a process which is only dependent on the elements contained in the original substance, but not on its molecular structure.

We took care that this effect is not due to rest-gas impurities, by using spectra from different laboratories with entirely different experimental setups in this respect. These series cannot be fragments because e.g. the ratio $C_{2n}/C_{2n}H$ is about the same for decane and fullerene with their very different (n_H/n_C) -ratios of 2.2, and 0, respectively. We give some reasons for the different abundances observed for the three series :

- The shape of the $C_{2n}H$ - series is different from the other two because one of the possible C-sites is already blocked so that the probability of further expansion of the chain is decreased.
- The C_{2n} - series has higher overall yields than the C_{2n+1} - series because the energy balance for the formation of the *even* chains is better due to a higher ratio of triple bonds, which are energetically favoured in the formation process.

Adiabatic Expansion Model for the Formation Process

We have done calculations based on the adiabatic expansion model, which qualitatively predicts the curves. Theoretically, we calculate the PDMS-abundance $f(g)$ for C_n for the ions coming from the innermost zone around the ion impact track by assuming a cylindrical area of hot and dense completely atomized matter at the beginning, which then is followed by an adiabatic expansion out of the primary impact hole. The sequential addition of Carbon atoms during the expansion leads to carbon-clusters, the formation of which is stopped when the density of the expanding material becomes too low. Modelling and simplifying to an analytical expression we get [1]

$$f(g) \approx g^{1/12} I_{1/4}(g^{2/3}/\sigma) \exp(-g^{4/3}/2\sigma)$$

where σ is an thermo-hydrodynamical integral but proportional to the monomer sticking probability, which we take to be proportional to the number of active ends of the molecule. The absolute amplitude of the three cases is taken to be 1 : 1/2 : 1/4 for $C_{2n}H$, C_{2n} , and C_{2n+1} , respectively.

References

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