

# Experimental and Numerical Study of Pentacene Molecular Beam Seeded in the Free Jet of Helium

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**Abstract.** A problem of increasing interest in the last years, both for mass-spectrometry and for deposition of organic semiconductor films, is to increase and control the flux of large organic molecules seeded in a carrier gas expanding towards a skimmer. This paper deals with experimental and numerical investigations on the dependence of kinetic energy of Pentacene molecules from the gas flow rate. Pentacene is a very important molecule in the field of organic semiconductors where it plays the role of a prototypical system for molecular electronics. The numerical results concerning the flow rate of helium through an optimized capillary as well as the kinetic energy of Pentacene molecules in the beam are in qualitative agreement with the results of measurements paving the way to the optimization of the device.

**Keywords:** Pentacene, free jet, seeded beam, kinetic energy, simulation.

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## INTRODUCTION

Supersonic beams of organic molecules are becoming of increasing importance in several fields such as the somewhat more conventional mass-spectrometric and spectroscopic studies, as well as in the more novel studies involving synthesis of thin films, because they give unprecedented control on parameters that result to be very important in particular for the growth and deposition on solid surfaces. The demand of sources well engineered to reproducibly give high and controlled flows of large organic molecules seeded in a carrier gas expanding towards a skimmer, is hence strongly increasing both for mass-spectrometry and for deposition of organic semiconductor films.

The main goal that one would like to address is to optimize the free jet expansion of the seeded precursors to best control their final energy state together with a well shaped beam profile. To this end, we describe in this paper experimental and numerical efforts to understand the dependence of the Pentacene kinetic energy from the driving pressure for a particular nozzle geometry. This is in fact crucial to better control the surface processes leading to molecular assembling at the different stages of a thin film growth. Original supersonic molecular beam experiments on Pentacene film deposition were carried out in IFN-CNR with the use of capillary to form the carrier gas flow. These pioneering studies have shown the importance of kinetic energy of the impinging molecules in thin film formation [1].

## EXPERIMENTAL SET-UP

Figure 1 shows the basic scheme of the deposition apparatus that has been used to both deposit the molecular films and simultaneously characterize the energy distribution of the species seeded in the supersonic beam.

The apparatus has been designed essentially in three stages of differentially pumped vacuum chambers in order to make compatible on one hand the large fluxes in the chambers where the beam is formed and skimmed with, on the other hand, the UHV conditions that are used in the deposition chamber needed in order to reduce to a minimum any possible contamination during the growth. The first vacuum chamber is the one requiring the largest pumping speed to evacuate the heavy gas load coming from the nozzle. The pumping speed used here is about 2000 l/s. The background pressure is about  $10^{-8}$  mbar which increases during source operation between  $10^{-5}$  and  $10^{-4}$  mbar. Up to three hyper-thermal supersonic beam sources, specifically designed for organic materials, can be housed in this first chamber. The sources can be heated and temperature controlled independently. After the expansion the beam enters the second chamber through a skimmer, placed at about 10 mm in front of the source, which also defines the geometry of the beam while ensuring the needed differential pumping in the second chamber. Different skimmer diameters ranging from 0.3 mm to 1.5 mm have been used depending on the type of the experiment. The skimmer can be heated up to about  $250^{\circ}\text{C}$  in order to avoid the deposition on its surface of molecular layers of increasing thickness that would modify the shape of the hole, interfering with the jet expansion, and finally could eventually clog it up. The second vacuum chamber allows both to differentially pump the system, eliminating the remaining excess of carrier gas, and to better define the beam geometry through a second skimmer. Here the background vacuum is typically in the  $10^{-8}$  mbar range while the pressure during beam operation increases typically in the range  $10^{-6}$  and  $10^{-7}$  mbar.

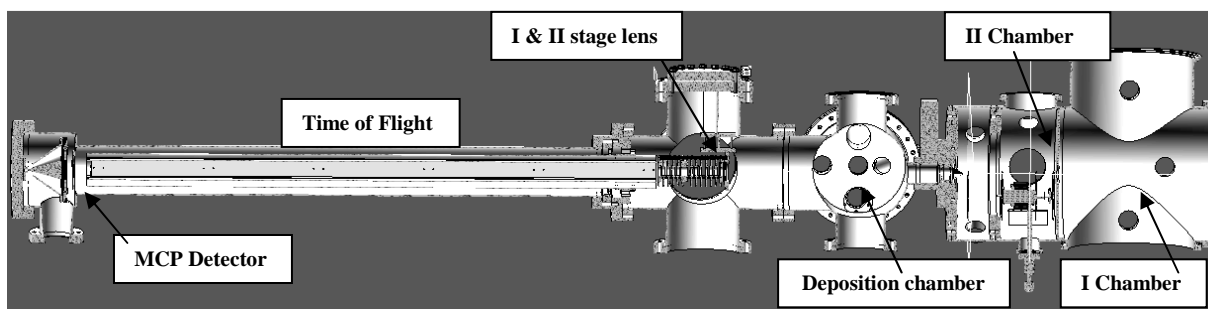


FIGURE 1. SuMBE Experimental Apparatus.

The third chamber houses the time of flight mass spectrometer (TOF-MS) used for the beam characterization, a microbalance, the sample manipulator and a spectroscopic ellipsometer. The in line configuration of TOF-MS allows collecting the mass spectra needed for characterizing the supersonic molecular beam. The molecular ionization is achieved by the fourth harmonic of a Nd::YAG laser or by using a tunable Titanium Sapphire laser including second and third harmonic generation. We use multiphoton ionization processes to achieve a very high sensitive, time resolved, soft detection of the molecular species. The system gives also on-line precious information about the purity of the beam, the presence of clustering, etc. The TOF-MS gives also, in this configuration, via a fitting procedure based on the instrument function carefully calibrated, the kinetic energy and velocity distributions of the molecules in the supersonic beam.

Figure 2 shows the hyperthermal supersonic beam source and its mounting. The set-up was specifically designed to produce supersonic molecular beam of organic materials. It consists of a quartz tube of about 1 cm of diameter and about 12 cm long. The nozzle, the most critical part of the whole source, is produced at the closed edge of the tube. Its size has been optimized in order to achieve, for our given pumping speed, the maximum forward flux together with best beam control and performance. The typical nozzle used is a cylindrical capillary, the length of which is about 3-4 times the diameter (60  $\mu\text{m}$ ). The raw organic material, usually in the form of a powder, is contained in an open capsule (made of quartz) positioned in the quartz tube close to the nozzle. The heating needed to purify and sublime the organic material is provided by two independent heating elements. The first one is a tantalum foil surrounding the quartz tube while the second one is a tantalum filament in a contact with the front edge of the quartz tube around the nozzle. Two thermocouples and appropriate feedbacks on the electrical power supplied to the heaters give the needed temperature control and stability to better than 1%. Our configuration allows an

adequate control on both seeding (degree of sublimation) and kinetic energy of the molecules in the beam. The empirically and experimentally optimized conditions are just the starting point for further improvements that could come from a better understanding of the working conditions. These further improvements could come from the modeling studies that are the subject of present work.

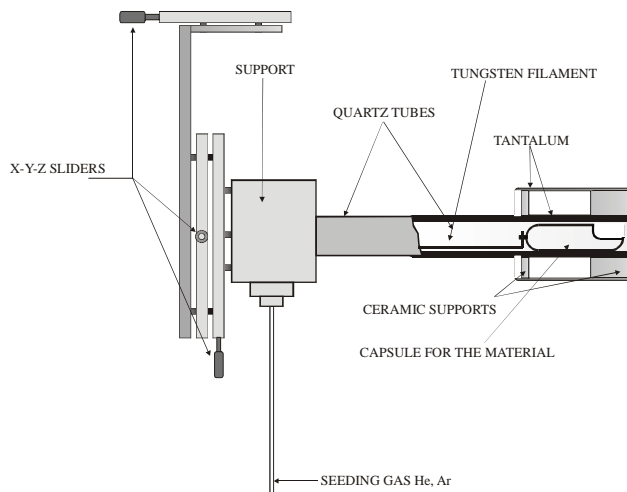


FIGURE 2. A schematic representation of the supersonic molecular beam source.

## Organic Supersonic Beam Characterization

As already mentioned, the major aims of the beam characterization are: 1- to determine the presence and hence minimize unwanted chemical species or processes such as dissociation and/or clustering (since in the experiment discussed here we addressed the growth in absence of clustering); 2- to measure the kinetic energy of the molecules and the degree of ro-vibrational cooling. To this end we systematically carried out TOF-MS studies via the photoionization of the species present in the beam. Figure 3 shows a typical TOF-MS spectrum obtained by photoionizing a supersonic beam of Pentacene seeded in He using the 4<sup>th</sup> harmonic of a Nd::YAG laser. The spectrum was measured after a period of several hours of out-gassing of the material in the source up to the point that no traces of solvents were anymore visible and only the peaks of He<sup>+</sup> (carrier gas) and of Pentacene molecules were visible.

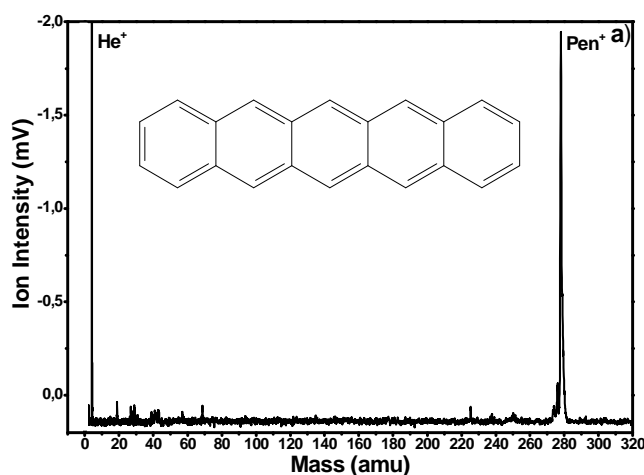


FIGURE 3. Typical mass spectrum of Pentacene molecules seeded in a He beam. The inset shows the molecular structure.

Using a computer code that accurately simulates the TOF-MS calibrated response, we could fit the peaks, positions, and shapes in order to obtain the kinetic energy distribution of the molecules. The limiting values, for a high carrier gas pressure, of such computer simulations are consistent with the formula [2] describing the kinetic energy due to the aerodynamic acceleration of the supersonic expansion of the molecules  $m_{or}$  in the much lighter carrier gas  $m_{av}$ :

$$E_{kin} = \frac{5}{2} \frac{m_{or}}{m_{av}} RT_{nozzle}$$

where  $R$  is the gas constant,  $T$  is the temperature and  $m_{or}$  and  $m_{av}$  are respectively the organic molecules and the average (organic molecules plus carrier gas) molar masses. Since the aerodynamic acceleration of the heavy molecules is due to the number of collisions with the atoms of the much lighter carrier gas there is a velocity slip between the two species that goes to zero as the pressure of the carrier gas is increased (dilution larger than  $10^{-3}$  or  $10^{-4}$  mbar).

## NUMERICAL SIMULATION

In the experiments described above the acceleration of Pentacene molecules was performed by seeding in helium as a carrier gas. The flow of helium was formed by a capillary nozzle with diameter ( $d$ ) in the range of 50 - 60 microns and a length ( $L$ ), of 4 - 5 diameters. For theoretical calculations the parameters of the capillary were set as follows:  $d = 55 \mu\text{m}$ ,  $L = 200 \mu\text{m}$ . The distance between the capillary exit and the skimmer inlet was 10 mm while the skimmer diameter was set to 0.5 mm.

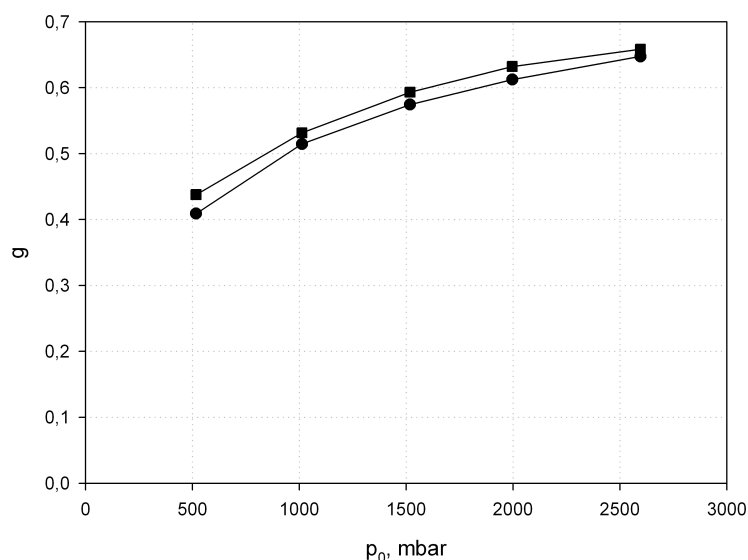
The numerical simulation of Pentacene motion in the carrier gas flow was divided into two separate stages. The first one consists in calculating the parameters of the main flow, representing the free jet of helium issuing into vacuum from the capillary. The choked flow in the capillary opened into vacuum was simulated by marching procedure in the frames of parabolized Navier-Stokes equations (PNS-algorithm) [3] under the assumption that the pressure in the cross section of the capillary is constant. At each computational step the pressure in the new section providing the constant radius of the capillary was determined. The parameter of this calculation is the flow rate of helium. A well-known property of such flows is the choked effect consisting in the fact that it is impossible, starting from a certain distance from the capillary inlet, to determine the needed pressure, that indicate the sonic state of the flow. If the position of such effect exceeds the actual capillary length, the value of the flow rate should be increased compared to the previously used one, and decreased in the opposite case. Then a new calculation is carried out with this new corrected value of the flow rate and the procedure is repeated for as long as the length of the capillary with choked flow at his exit will equal its real length. This approach to the calculation of gas flow through a capillary, opened into the vacuum, has been tested on several variants by modeling the flow in the frames of the full set of unsteady Navier-Stokes equations that were solved numerically by original algorithm, based on a staggered grid (NS-algorithm) [4]. In this approach, there is no need to specify the gas flow rate since it is automatically determined during the simulation. The results obtained by these two approaches were found to be in good agreement with each other. These calculations give the distribution of the parameters on the capillary exit, being the starting surface for further calculation of the flow in the free jet behind the capillary, opened into vacuum. This calculation is also performed in the frames of parabolized Navier-Stokes equations [3], with the effect of viscosity and thermal conductivity of gas being not taken into account, that should not greatly affect the flow in the absence of the solid surfaces in the flow field. Modeling of flow in the jet in the frames of full set of Navier-Stokes equations is impossible due to their limited applicability to describe the expanding hypersonic flows. In principle, this flow can be calculated by DSMC-method [5], however, large statistical scatter of flow parameters in the vicinity of the axis, typical of axisymmetric flows simulated by the DSMC-method, would lead to unreasonably long computer resources for a too wide scattering of the results, important for the interpretation of molecular beam experiments, operating with the small diameter of the skimmer inlet orifice.

The final stage of the calculation is to simulate the motion of Pentacene in the jet flow field of helium. As for typical experimental conditions the concentration of the Pentacene in the flow is small, we can neglect their influence on the flow of carrier gas, and simulate their movement in the frames of a linear Boltzmann equation, i. e. for known distribution of the parameters of the main flow. An effective method for solving a linear Boltzmann equation is the well-known test particle Monte Carlo method, the main features of which are described in [6, 7]. To apply this method, a molecular model describing the Pentacene-helium collisions should be specified. The choice of

molecular models, adequate to the structure of Pentacene, is not an easy task. This molecule,  $C_{22}H_{14}$ , with the chemical structure shown inside Fig. 3, is of a rather flat rigid shape, containing five rings. A full account of the molecular structure in a model of its interaction with helium appears now unrealistic. In this study we adopted a model with a spherically symmetric repulsive intermolecular potential, while we consider two extreme cases of possible potentials, namely, the model of hard spheres (HS-model), the most rigid, and the model of Maxwell molecules (MM-model), the most soft. With all the uncertainties discussed about the need of a more realistic interaction potential, the experimental results should be located within the "fork", formed by these two extreme cases considered. The cross section for Pen-He collisions for HS-model was estimated on the basis of data for heavy hydrocarbon molecules [8] and was found to be about  $186 \times 10^{-16} \text{ cm}^2$ .

For polyatomic Pentacene with large number of internal degrees of freedom the model for relaxation of internal energy of the molecule in a collision with helium is important. To describe this inelastic process the known Bornakke-Larsen model [5] was used, assuming that all internal degrees of freedom whose number is equal to  $3N - 3 = 105$  ( $N = 36$  - number of atoms in the molecule) have the same temperature. The fraction of inelastic collisions is taken to be  $1/Z$ , where  $Z$  - is a parameter, which should be selected on the basis of comparison of predicted and measured values of internal energy. In the first stage of the calculations we have adopted the value of  $Z = 1$ , i. e. assuming all collisions to be fully inelastic.

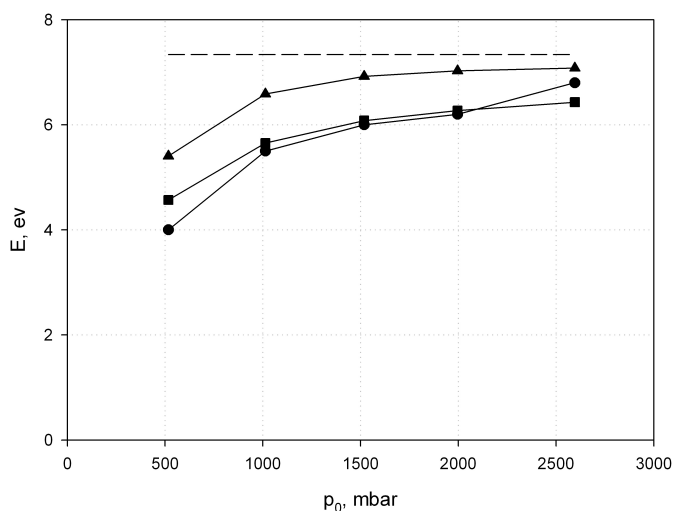
## RESULTS AND DISCUSSION



**FIGURE 4.** Measured (squares) and predicted (circles) dependencies of flow rate discharge coefficient on stagnation pressure.

Fig. 4 illustrates the dependence of flow rate of helium with respect to the experimental conditions ( $T_0 = 490 \text{ K}$ ). Results are presented as the dependence of the flow rate discharge coefficient on the stagnation pressure. As shown in the figure, the calculated results agree well with experimental data. There is no doubt that there could be a small mismatch due to the accuracy of the parameters characterizing the capillary ( $d, L$ ), an almost complete agreement between the calculated and experimental data could otherwise be achieved.

Fig. 5 illustrates a comparison between calculated and experimental dependencies of the kinetic energy of Pentacene at the position corresponding to the skimmer inlet orifice. Calculated curves are given for the two molecular models used to describe the Pen-He collisions. The data for equilibrium flow i. e. without velocity slip between Pentacene and helium flow, representing theoretically maximum possible kinetic energy of Pentacene, are also shown for comparison. The figure shows that the calculated and experimental data are in qualitative agreement: with increasing stagnation pressure the kinetic energy of Pentacene also increases because of the greater number of collisions in the flow, which reduces the slip between the components of the mixture. The experimental data are in good agreement with calculated ones obtained with the HS-model.



**FIGURE 5.** Mean kinetic energies of Pentacene as a function of stagnation pressure at the position of the skimmer orifice: comparison between experimental data (circles) and theoretical predictions of two molecular models (MM – triangles, and HS – squares) and the data for equilibrium flow i. e. without velocity slip between Pentacene and the flow of carrier gas (dashed line).

## CONCLUSION

The simulation carried out and the comparison with the experimental data shows the feasibility of modeling the supersonic expansion of large organic molecules seeded in He supersonic beams. The good agreement achieved is very sensitive to the geometry of the nozzle and the geometry of the nozzle-skimmer assembly as well as to the experimental conditions. We are hence convinced that by future work, based on such modeling, we could strongly improve control and performance of the sources. The modeling can hence guide the engineering of better performing sources that could be tailored for achieving the wanted conditions to produce organic films layer with the desired properties.

## ACKNOWLEDGMENTS

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