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QUANTUM
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Cold Beams of Biomolecules for Quantum Optics

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Abstract. We study laser desorption into an adiabatically expanding atom beam as a promising technique to volatilize an ensemble of cold biomolecules. Samples under investigation are the amino acid Tryptophan and the polypeptide Gramicidin. We discuss the possibilities of such beams for applications with respect to matter wave interferometry.

Keywords: molecular beams, matter waves, cold molecules
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1. Introduction

The generation of beams of neutral large clusters or molecules is of interest for a number of fundamental quantum experiments [1–4], for applications in high resolution spectroscopy [5, 6], metrology [7–9], cooling [10, 11] and trapping [12, 13] as well as for molecular optics [14].

The volatilization of biomolecules is a common need and challenge for various other fields of science, too. It is by now well known that even thermolabile molecules can be brought into the gas phase using techniques such as matrix assisted laser desorption ionization (MALDI) [15, 16] or electrospray ionization (ESI) [17]. They have become standard tools for physical chemistry and biology. Our experimental assessment of these methods for quantum optics applications [18,19] shows however, that variants of direct and matrix-free laser desorption might be more favorable in all those experiments which require neutral instead of charged beams — a condition which applies for instance to matter wave interferometry.

Here we discuss the generation of cold molecular beams using laser desorption from a pure sample of biomolecules seeded into an expanding noble gas jet. This allows us to obtain translational temperatures in the beam as low as a few Kelvins.

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The combination of pulsed laser desorption with cooling by a supersonic expansion of a monatomic carrier gas has already been extensively studied within the framework of physical chemistry [20–22]. Here we analyze the use of such beams in particular for experiments which aim at probing the wave-particle duality of large organic molecules in matter wave experiments based on diffraction at mechanical gratings. We show that sufficiently intense beams can be created at translational temperatures of below 20 K. Also the internal temperatures are much reduced which helps minimizing the influence of decoherence which might otherwise for instance be mediated by the emission of thermal photons [4].

2. Experimental Setup

Our source consists of a laser desorption unit to vaporize the molecules and a fast valve to release a cooling noble gas pulse over the desorbed hot molecules. The gas pulse carries the biomolecules over about half a meter into the detection stage, where they are ionized by a UV laser pulse. The ions are then detected and mass analyzed in a linear time-of-flight mass spectrometer.

Two different desorption designs were used in our experiments. In the first setup (D1) the molecules were initially spray-coated on top of a 100 mm long polished metal substrate, which was positioned very close to the nozzle exit. Every few desorption pulses the sample is shifted by a stepping motor to expose a fresh desorption spot. The volatilized molecules are then entrained by a freely expanding supersonic gas jet, which is released from a pulsed solenoid valve (General Valve 99). The nozzle has an opening of 0.5 mm and could be cooled to 150 K in thermal contact with a liquid nitrogen cooling system.

In the second setup (D2) molecular powder was pressed on a finely threaded rod. The laser then desorbed the molecules directly from the screw, which was continuously rotated to expose a fresh sample position for each desorption event. This design allowed the preparation of thick layers and thus longer operation times. Here the gas pulse emerged from an electro-magnetic pin hair valve (Jordan Inc.) followed by a 2 cm long mixing channel with a diameter of 2 mm to improve the thermalization between the molecules and the carrier gas [23]. In setup D2 the opening time of the valve was as short as 480 μs and in setup D1 the valve opened for 300 μs, which allows to keep the base pressure in the preparation chamber at about 10^{-5} mbar.

Arrangements similar to our setups D1 and D2 were also compared by Tarbutt et al. [24] for the formation of the diatomic YbF molecule. In our case the internal complexity of the particles poses some additional constraints. The design D1 allowed a free (but short) supersonic expansion in contrast to the extended mixing in design D2. In our experiments D1 turned out to be favorable for obtaining very low temperatures for the amino acid Tryptophan, while setup D2 was successful in obtaining a strong, but translationally warmer, signal of the polypeptide Gramicidin D, which is composed of 15 amino acids.

In both experiments, the desorption is done using a frequency tripled Nd:YAG laser (Brilliant, 355 nm, 5 ns) which is usually operated at energies between 0.5 and 6 mJ and focused to a diameter of about 300 μm.

The seeded molecular beam traverses a skimmer of 1 mm diameter when it passes into the analyzing chamber. The pressure in the detection region therefore never exceeds 10^{-6} mbar. The experiment usually operates at a repetition frequency of 10 Hz in order to keep the base pressure low. The neutral molecules are multiphoton ionized by a pulsed UV laser beam (266 nm, 7 ns, 0.5–4 mJ) and then identified in a linear time-of-flight mass spectrometer (Kaesdorf, München).

3. Formation of a Cold Beam

Adiabatic expansion is a well established cooling method in molecular beam experiments [23]. The cooling affects the translational, rotational and vibrational degrees of freedom — although with different efficiencies. For molecule interference experiments the translational temperature is the most important parameter, since it determines the de Broglie wave length and the spectral purity of the matter waves. But also the internal temperatures are relevant for complex particles, since they determine for instance thermal emission processes, conformation changes, the molecular alignment and much more.

The temperature T of the expanding atoms is described by the Poisson equation [23]: $T/T_0 = \left(1 + M^2(\gamma - 1)/2\right)^{-1}$, with the Mach number $M = v/c$ defined as the ratio of the beam velocity v to the local speed of sound c. Of equal importance is the terminal velocity, i.e. the beam velocity in the lab frame, after the adiabatic expansion process. This is given by $v_f = \sqrt{2k_BT/m}\sqrt{\gamma/(\gamma-1)} = v_{mp} \cdot f_c$. The adiabatic coefficient γ and correction factor f_c take on the values $\gamma = 5/3$ and $f_c = \sqrt{5/2} \simeq 1.6$ for monatomic noble seed gases. The adiabatic expansion has therefore a dual character for our purposes: on the one hand it is much needed to provide the internal cooling which prevents the biomolecules from thermal fragmentation. On the other hand, the speed of the carrier gas will also be imposed on the analyte molecules — except for a velocity slip for very massive analyte particles.

Since noble gases may reach Mach numbers as high as $M \sim 10$–50 when expanded from atmospheric pressure into vacuum, the final temperature may actually be a factor of ten lower than the nozzle temperature. This effect significantly increases the stability of the embedded thermolabile molecules, which would otherwise disintegrate within a short distance behind the nozzle. It also allows to improve the molecular collimation as well as the phase space density: the narrowing of the velocity spread corresponds to a signal gain in a certain velocity interval. From the equation above we see that the molecular temperature may be varied by using either different seed gases or different nozzle temperatures.

4. Results

Figure 1 shows a typical mass spectrum of Tryptophan obtained in setup D1. The high signal to noise ratio was already obtained after integration over 30 shots (3 seconds). We clearly identify the mass peak of the intact molecule at 204 u. The absolute signal as well as the signal to noise ratio of 410:1 are promising for interference experiments as outlined further below. We also recognize a typical fragment peak at 130 u which might be generated either in the desorption or in the ionization stage. It is interesting to note, that a matter wave interferometer with these particles will allow us to sort out the respective contribution of both processes since the interference fringe visibility depends on the de Broglie wavelength and therefore on the mass [25,27]. Fragments created in the source or in the detection stage will be identifiable by their different interference visibilities. The peak at mass 92 u can be assigned to Toluene, which was used for calibration.

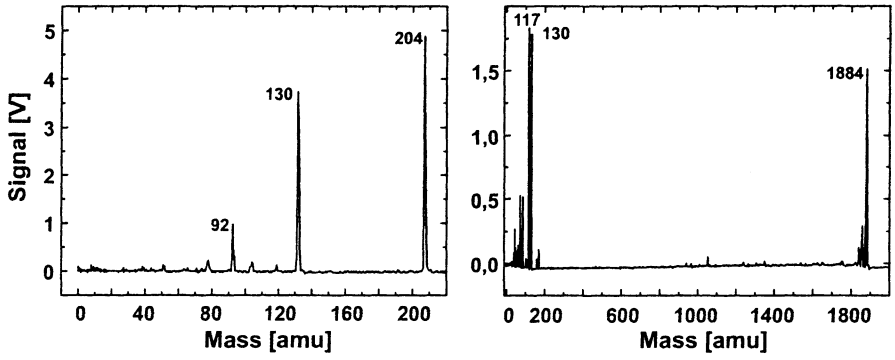

Fig. 1. Left: Mass spectrum of Tryptophan. The intact molecule can be well separated from the two major fragments. Right: Mass spectrum of Gramicidin and its fragments

Similarly, we studied Gramicidin in setup D2 and we observe a narrow peak at $m = 1884$ u in the mass spectrum of Fig. 1 (right). This can be unambiguously assigned to the intact polypeptide. Also here, we recognize small fragments which we can ignore as an interference experiment could simply operate at a fixed mass. We could not observe any intact Gramicidin in our setup D1. This indicates that the internal cooling and thermal stabilization of the polypeptide requires the increased number of collisions in the mixing channel. The channel design D2 was less effective in translational cooling, since lower translational temperatures can be achieved for Tryptophan in the free expansion of setup D1.

The translational temperature of the analyte molecules can be determined by measuring their time of flight. The timer is triggered by the 5 ns desorption laser pulse and stopped by the ionizing UV laser pulse. Since the typical travel times are of the order of 1 ms (50 cm at 500 m/s) the finite width of the light pulses are completely negligible.

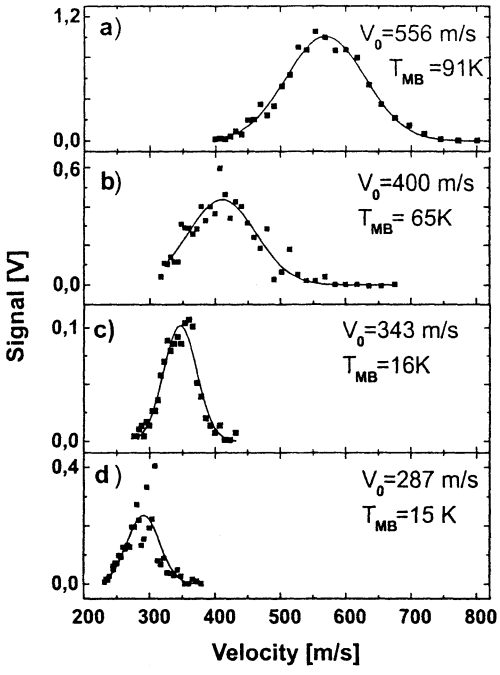

Fig. 2. Velocity distributions of Tryptophan under different expansion conditions. Values specify the most probable velocity and the translational temperature for a) Argon as a carrier gas at $T = 300$ K nozzle temperature, b) Xenon at $T = 300$ K, c) Argon at $T = 170$ K, d) Xenon at $T = 200$ K

In Fig. 2 we show some experimentally determined velocity distributions and we fit them with a Maxwell–Boltzmann function to derive the translational temperature ($f(v) = aT^{-3/2}v^2 \exp\{-(m(v-v_0)^2)/(2k_BT)\}$). The value thus obtained is actually an upper bound for the temperature since any thermal delay in the desorption process would introduce a broadening of the distribution function.

The observed average velocities are in very good agreement with the calculated velocities for the free expansion of the carrier gases. The desorbed Tryptophan is therefore in thermal equilibrium with the carrier — at least in the translational degrees of freedom. The lowest temperature that we reach with Xenon at 200 K amounts to only 15 K. This is in good agreement with earlier results for similar molecules in this complexity range [20]. We therefore expect in analogy with these studies, that also the rotational and vibrational temperatures are equilibrate to 10–30 K. This is low enough to guarantee the population of the lowest vibrational modes in Tryptophan.

5. Laser Desorbed Biomolecules in Matter Wave Interferometry

In order to use biomolecules in an interferometer with material gratings it is important, that the gratings do not cause any fragmentation of the labile particles. In order to test that, a SiN_x grating with a grating constant of 257 nm and openings of

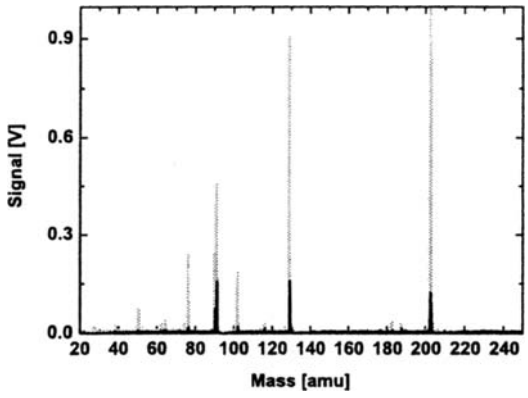

Fig. 3. Tryptophan mass spectrum before (grey line) and after (black line) passage through a SiN_x nanograting. The attenuation by the material structure does not create any measurable fragmentation of the amino acid

100 nm (wall thickness 160 nm) was inserted into the molecule beam. The comparison of the mass spectrum with and without grating is presented in Fig. 3 and shows that fragmentation can be completely neglected. The relevance of internal state changes is however, still an open issue for future experiments. One might actually hope to reveal such events as a change of the molecular polarizability which can also be detected with high accuracy inside a molecule interferometer [26]. As far as the flux is concerned, the combination of two such gratings and one optical phase grating would reduce the signal by a factor 100, which would still leave a sufficiently high signal for interferometry with Tryptophan.

One should note that the observed signal is intrinsically selected from a very narrow velocity band of better than $\Delta v/v = 1\%$ because of the pulsed desorption and detection. Together with as mass resolution of better than 1:100, also the Broglie wavelength can be defined (a posteriori) to better than one percent. In addition to this very good velocity selection, also the mean velocities in the new source are suitable for a Talbot Lau interferometer [27], as shown in Fig. 4.

The Talbot length $L_T = g^2/\lambda_{dB}$ with $\lambda_{dB} = \hbar/mv$ then defines roughly one half of the interferometer length, which is currently limited to 0.8 m by the present vacuum chamber. In a larger lab this dimension could be stretched but one should then also be aware of the increasing influence of several dephasing mechanisms [28].

Figure 4 shows that any polypeptide up to the mass of Insulin B ($m = 3496$ u) still fits to a near-field interferometer with such small gratings, even at the rather high average velocity of 500 m/s.

Interferometry with such complex molecules is accompanied by several further requirements. For instance we are currently implementing a new interferometer which utilizes an optical phase grating [27,29] that allows to circumvent the influence of the van der Waals force between the grating walls and the highly polarizable biomolecules. Also, thermally activated conformation changes in free flight are an interesting internal degree of freedom that will have to be cooled/controlled in the future.

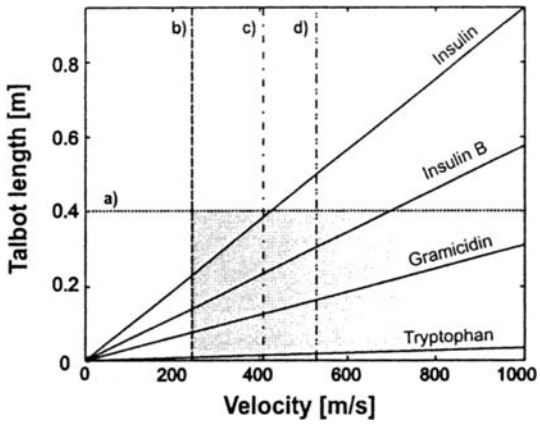

Fig. 4. Boundary conditions on molecule velocity (horizontal axis) and interferometer size (vertical axis) for a grating constant of 257 nm. a) Upper limit for L_T in our current experimental setup. Vertical lines indicate the mean velocity of an adiabatically expanding jet with b) Xenon at 180 K, c) Xenon at 300 K, d) Argon at 300 K

Insulin, with a mass of 5733 u, would still be a good candidate in such a setup. The required velocity below 400 m/s can be simply set by choosing a heavy carrier gas in the adiabatic expansion. The efficient detection of neutral molecules in this mass range is again an open field for interesting future research.

In summary, laser desorption into a carrier gas has been shown to be a suitable tool for bringing thermolabile molecules in sufficient amounts into jets of sufficiently low translational temperatures. Whether this method can be extended for much beyond $m = 10.000$ u remains still to be shown. This will certainly also depend on further improvements on the detector side. At any rate the developed source is very promising for matter wave applications with large polypeptides and probably for small proteins in the near future.

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