A superconducting NbN detector for neutral nanoparticles

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Abstract
We present a proof-of-principle study of superconducting single photon detectors (SSPD) for the detection of individual neutral molecules/nanoparticles at low energies. The new detector is applied to characterize a laser desorption source for biomolecules and allows retrieval of the arrival time distribution of a pulsed molecular beam containing the amino acid tryptophan, the polypeptide gramicidin as well as insulin, myoglobin and hemoglobin. We discuss the experimental evidence that the detector is actually sensitive to isolated neutral particles.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The detection of isolated neutral molecules and nanoparticles in the gas phase is both a necessity and a challenge for many experiments that range from physical chemistry to environmental monitoring [1] to the foundations of physics. Our own work was originally motivated by matter wave interferometry with massive molecules [2–4] and applications in molecule metrology [5, 6]. The extension of such experiments to higher masses also requires improved methods for detecting neutral nanoparticles. While ionization techniques are routinely used for particles up to about 2000 Da, post-ionization of organic molecules beyond that mass has remained a significant challenge [7, 8]. Recent experiments observed photoionization of tryptophan–metal complexes and nucleotide clusters up to 6000 Da [9, 10]. But for the majority of high-mass biomolecules this method seems to be precluded.

Hyperthermal surface ionization [12] was shown to allow the detection of some neutral molecules, with insulin currently setting the mass record [13].

Modern nanofabrication technologies also allow the building of nanoscale oscillators which change their resonance frequency when their mass is augmented by even a single molecule. Such cantilever based detectors [14, 15] have a lower rather than an upper mass limit. They currently reach a sensitivity of below 200 Da [16]. The first proof-of-principle mass spectrometer applications showed the capability to detect single proteins [17].

Whenever mass cannot be measured directly, bolometer detectors [18–20] may convert molecular energy first into sensor temperature and then into an electrical signal. However, the translational energy of a single amino acid, such as tryptophan, does not exceed 0.3 eV, even at a molecular velocity of 500 m s⁻¹. This is why the first bolometers [21] still operated with a minimum detection threshold of about 10⁷ molecules s⁻¹. Superconductors were suggested as promising sensors [22, 19, 23] since their conductivity changes strongly with temperature in the vicinity of the phase transition edge.

The implementation of superconducting tunneling junctions (STJ) made it possible to detect charged individual molecules [24–26]. This is interesting for mass spectrometry, because the STJ response depends on the particle’s energy [27]. This allows us in principle to combine the mass discrimination of a time-of-flight spectrometer with a detector whose efficiency remains constant over a wide mass range. Tunneling junction detectors, however, require cooling well below 4 K and up to now they have only been used for recording either
ensembles of slow neutral particles or for detecting individual but energetic charged particles.

In this paper we present our first experimental evidence that a combination of both is feasible, i.e. a detector for single neutral molecules of low kinetic and low internal energy. Our nanowire detector was originally fabricated as a superconducting single photon detector. Its sensitivity to single photons was demonstrated across the entire spectrum from UV to mid-IR, with quantum efficiencies up to 30% [28–32]. Before we started the experiments, it was far from obvious that such a device would also be sensitive to slow nanoparticles. In the following we discuss the acquired evidence that this detector is capable of recording the incidence of isolated neutral biomolecules.

2. Experimental setup

The experimental setup consists of a pulsed molecular beam, a free flight trajectory in high vacuum and the superconducting nanowire detector in a differentially pumped helium cryostat, about 76 cm behind the source.

2.1. Superconducting detectors

Two different types of detector were tested: superconducting single photon counting devices (SSPDs) and superconducting bolometers (SBs).

The SSPDs were fabricated by depositing a NbN film of 3.5–4 nm thickness on a sapphire substrate. We tested chips with an open area of either $10 \times 10$ $\mu$m$^2$ or $20 \times 20$ $\mu$m$^2$. The 100–120 nm wide superconducting wire meanders on the surface with a filling factor of 60%. The critical temperature of NbN is $T_c = 10–11$ K and the critical current density amounts to $j_c = 3.5 \times 10^6$ A cm$^-2$.

The SSPD fabrication process was described in detail elsewhere [33]. In brief, NbN superconducting films were deposited on R-cut sapphire substrates by DC reactive magnetron sputtering in an Ar and N$_2$ mixture. The film was patterned by direct electron beam lithography and reactive ion etching. Gold contacts were added using photolithography and wet etching. In figure 1(a) we show electron microscopy images of the sensitive element. We operate the device in a liquid helium bath cryostat at 4.2 K and apply a DC bias current slightly smaller than the critical current. The signal is capacitively coupled from the chip to the oscilloscope.

The detection mechanism may be understood as follows: when a molecule hits the film surface, it creates high-energy acoustic phonons. These phonons are rapidly absorbed by the electron subsystem of the film due to their short inelastic mean free path. Excess quasiparticles are then created which, in turn, dispose of their energy by the emission of second generation phonons. This triggers an avalanche multiplication cascade. The process is similar to what happens during photon detection. The distinctive difference lies in the first step: the photon detection cascade starts from a single high-energy quasiparticle created by the photon. The dynamics of the subsequent stages is determined only by the absorbed energy.

When the energy of the quasiparticles decreases to a value around 10 K, the electron–electron interaction becomes more efficient for the multiplication of the quasiparticles than the electron–phonon interaction. Due to this fact, the main part of the energy that is initially deposited in the film remains in the quasiparticle subsystem. At the end of the cascade, a hot spot of excess quasiparticles is formed and the supercurrent is forced to flow around the new normal-conducting area. If the hot spot is sufficiently large the current density in the ‘sidewalks’ increases beyond the critical current density. This results in a short breakdown of superconductivity across the entire width of the nanostripe and in a voltage pulse that can be easily detected [28–31]. For photons, a typical pulse response lasts over 10 ns.

The second detector type that we tested was a classical superconducting bolometer. These chips were made from the same NbN film, again using photolithography and wet etching. Figure 1(b) presents a sketch of its sensitive element and an SEM image. The bolometer chip is working at the critical temperature $T_c$. The additional energy delivered to the surface by the impacting molecules may heat the superconductor above $T_c$ and cause a voltage peak. The incident energy has to be sufficiently high to induce the required temperature change. Because of the large width of the stripes this condition can often not be met by a single molecule alone and the sensors respond only to many simultaneously impacting particles. With this second detector type we were not able to detect any molecular signal in our experiments. This type of superconducting wide-area bolometer is therefore not discussed further in the following where we rather focus on our explorations of nanostructured SSPD chips.

2.2. Molecular beam source

The details of our laser desorption source have already been described elsewhere [9, 10]: organic molecules were laser
desorbed by a Nd:YAG laser beam (355 nm, 5 ns, 6–10 mJ), which was focused to a spot on a pressed powder sample (figure 2). The desorbed molecules are cooled and entrained by a jet of helium gas that fills the mixing channel before it exits through a 1 mm opening into a vacuum of $10^{-3}$ mbar. About 2 cm behind the mixing channel the beam passes a skimmer of 1 mm diameter, which separates the source from a differential pumping stage. In this second chamber the molecular beam is filtered by a copper mesh with 7.5 $\mu$m openings. This microstructure is used to reject grains of powder that might be ejected during the ablation process.

The stream of single molecules as well as possibly a background of microscopic particles leaves the second pumping stage through a 1 cm diameter opening into the detection chamber where the SSPD chip is attached to a helium bath cryostat. The overall distance from the desorption spot to the superconducting chip is 76 cm. For some experiments we added a second mechanical filter: a SiNx line grating with a period of 266 nm and openings as small as 90 nm was attached to the entrance window of the cryostat. This addition further limited the transmitted particle size and also helped to extend the lifetime of the SSPD chips, which was otherwise strongly affected by the accumulation of molecular material. Even with the additional filter in place, the active time of an individual chip was limited to about 20,000 desorption shots, after which time a layer of molecules had covered the surface and made it insensitive. It is known [11] that SSPD chips can even be used to resolve the energy of incident photons. Similar energy dependent measurements with molecules were, however, still impeded in our present proof-of-principle study by the time-varying surface coverage.

3. Results

In order to explore its detection capabilities the SSPD chip was placed into the laser desorbed biomolecular beam. The first experiments were performed with a mixture of several molecules containing 0.2 g myoglobin (17 kDa), 0.3 g $\beta$-carotene (537 Da), 0.3 g insulin (5.8 kDa), 0.25 g bovine serum albumin (BSA, 66 kDa) and 0.5 g cellulose of unspecified chain length to mechanically bind the other components.

In this first test we used a $20 \times 20 \mu m^2$ SSPD chip and in figure 3 we show a typical individual detection event from the desorbed molecule mixture. The peak is about 10 ns wide (FWHM) and indicates a high temporal detector resolution also for neutral nanoparticles. The peak is about 10 ns wide (FWHM) and indicates a high temporal detector resolution also for neutral nanoparticles.

We performed several tests to corroborate the evidence for the SSPD’s sensitivity to isolated molecules and to exclude other possible reasons for the observed signals such as for instance the co-propagating seed gas or co-desorbed cellulose. The influence of the rapidly expanding seed gas can be tested by switching off the desorbing laser beam. We searched...
for signs of the expanding helium carrier gas pulse alone, and the complete absence of any signal in this setting indicates that the SSPD chip is not capable of detecting individual helium atoms. The same is also true for all of the heavier noble gases such as neon, argon, krypton or xenon. None of them showed any detectable signal under our experimental conditions.

One might speculate that the higher kinetic energy of the more massive biomolecules could be outweighed by the larger number of lighter noble gas atoms. This argument would be supported by the fact that seed gas atoms must be much more abundant than the laser implanted biomolecules—otherwise supersonic expansion would never occur. However, since no signal was detected for the pure noble gas beams alone, a collective effect by the dense gas jet can be excluded. Since the biomolecular beam is more dilute than the carrier gas, a collective effect of organic particles is even less likely.

This finding is at variance with that for classic bolometers where the incidence of many particles is actually required to trigger a signal [21]. It has, however, to be noted that these detectors were not nanostructured and they were exploiting a different mechanism. Our result thus gives the first evidence that the SSPD chip is indeed not sensitive to the intense particle flux of atoms but rather to the local energy density of single complex nanoparticles.

As mentioned before, the molecules were always admixed with cellulose to achieve mechanical stabilization of the sample. In order to separate matrix signals from analyte signals we also performed a separate desorption experiment with pure cellulose powder alone. The complete absence of any measurable signal indicates again that the ablated matrix particles do not contribute any background in the SSPD counter. In order to enable a more quantitative evaluation we switched to a pulse counting mode and recorded time-of-flight curves for various experimental settings. The molecular velocity may differ from that of a free supersonic expansion, since the molecules can be delayed inside the gas mixing channel before they exit. This delay may lead to an underestimation of the actual velocity. The velocities and kinetic energies below are therefore reasonable lower limits.

In all the following experiments the samples contained only biomolecules from one species mixed 1:1 with cellulose.

In figure 4(a) we show the arrival time distribution for tryptophan (204 Da) and gramicidin (1.9 kDa) samples, respectively. Figure 4(b) depicts the distributions for insulin, myoglobin and porcine hemoglobin (66 kDa) samples. All curves in figure 4 were recorded using the same 20 μm × 20 μm SSPD chip, the same discriminator level, a bias current of 20±1 μA and two particle filters in the beam line, i.e. a 7.5 μm mesh as well as the 90 nm SiN filter. The opening time of the valve was set to 700 μs for all recorded curves in figure 4, except for that of tryptophan as discussed below. The arrival time distributions in figure 4 show a double structure which is a result of the particular valve setting in these experiments.

The agreement of the detected arrival times with the expected flight times may already be interpreted as a good indication for the detection of neutral particles. It is, however, desirable to corroborate this statement by complementary measurements which must rely on alternative detectors. As they are not readily available in the mass range beyond 2000 Da, where ionization detectors start to fail [7, 8] and nanomechanical detectors are not yet commercially available, it is also still unknown whether high-mass molecules (e.g. hemoglobin) can survive the desorption process as intact particles or whether the observed signals are rather caused by smaller neutral fragments generated in the source.

This is why our first checks were focused on characterizing the molecular beam source for tryptophan and gramicidin, where it is known [34, 35] that VUV laser ionization is soft and capable of detecting isolated molecules as well as larger clusters [9, 10]. A F₂ laser (157 nm, 5 ns, up to 3 mJ) is here combined with time-of-flight mass spectrometry (TOF-MS) to reveal the arrival time and mass distribution of all molecules emerging from the source.

Figure 5 shows a representative arrival time distribution for tryptophan, measured using TOF-MS and the same source settings as in the SSPD experiments. The flight distance between source and detector was shortened to 0.5 m. This also reduces the molecular flight times.

The arrival time distribution, recorded in photoionization TOF-MS at the mass of the single monomer (figure 4), has the same structure as the signals recorded by the SSPD (figure 5). Small differences in the arrival times can be assigned to

![Figure 4](image-url)
Time [ms]
Signal [a.u.]

Figure 5. Arrival time distribution of tryptophan recorded via laser post-ionization and time-of-flight (TOF) mass spectrometry. The shape of the TOF distribution reproduces the distribution recorded by the superconducting chip (see figure 4).

Figure 6. Arrival time distribution of gramicidin for different valve opening times, using a 10 μm × 10 μm SSPD chip. A reduction of the valve opening time leads to shifted arrival time distributions (slower molecules).

an accidental reduction of the valve opening time which influences both the pressure inside the mixing channel and the velocity of the expanding molecules. This is supported by figure 6, which depicts the arrival time distribution for gramicidin for three different valve opening times recorded by the SSPD chip. For short pulse times (figure 6, top) the arrival time distribution resembles the one recorded for tryptophan in figure 4(a), where the molecule arrival time was delayed. Interestingly, valve times around 600 μs do not show the double structure, as can be seen in figure 6 (center). We chose a slightly higher opening time of 700 μs (figure 6, bottom) for our experiments. This causes a double peak in the arrival time but also adds to the signal.

From these tests we gather the general insight that the arrival time distributions are rather identical for both the SSPD and the ionization detector. They are both consistent with the arrival of individual molecules. The absence of any signal related to the individual carrier gas atoms hints at an energy threshold in the SSPD which can only be overcome by sufficiently massive and energetic molecules. In our experiments the least energetic molecules detected by the SSPD were tryptophan particles in the velocity band of 300–500 m s⁻¹, i.e. with a kinetic energy of 100–300 meV if we assume we are seeing isolated molecules.

Compared with that value, all rare gas beams still have too little kinetic energy to be detected. Helium at 800 m s⁻¹ reaches only 10 meV and xenon at 250 m s⁻¹ would only attain 40 meV—still well below the value for tryptophan, which carries internal energy in addition.

4. Conclusion

The present experiments are just the promising start of an interesting journey into single neutral molecule detection using SSPDs. Our experiments give good first evidence that SSPDs can be used to register the incidence of neutral single nanoparticles.

As of today there is no efficient easily implemented way of detecting neutral large proteins to cross-check our results with individual, isolated insulin, hemoglobin or myoglobin. But we see a good consistency between the SSPD results and photoionization mass spectrometry in the flight times for tryptophan and gramicidin.

One might furthermore ask whether a high internal excitation may also add sufficient energy to the chip, which will be tested in future experiments by systematically varying the internal temperature of the molecules.

The possibility of detecting more massive neutral and labile molecules is promising for many applications in physical chemistry and also for matter wave interferometry. Even if the SSPD method cannot (yet) discriminate between different masses, de Broglie interferometry itself has been shown to be capable of discriminating different molecular properties [5] and experiments with clean and mass selected sources would only require a good sensitivity to the existence, not to the mass, of the particle.

The technology certainly requires further development and exploration but it may allow us to close a ‘detector loophole’ for particles which are too complex to be efficiently photoionized and yet too small to be well detected by other means.

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