Caging atoms for a better atomic clock

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1. Introduction

For the arctic explorer Fridtjof Nansen, 13 April 1895 had started well. Six days earlier, he had set a new record for the closest approach to the North Pole, and now he was moving quickly over unbroken sea ice towards Cape Fligely and home. But then came a sickening realization: in his eagerness to break camp, he had forgotten to wind the expedition chronometers. He had lost track of precise time, and with it of his longitude. Although his error could not have been more than a few minutes, it had long-lasting consequences. Forced to take a circuitously conservative route to avoid being swept into the North Atlantic, his expedition endured a hungry winter, camped on an unknown shore. Not until June the following year did he encounter other explorers and learn his true position on Northbrook Island in Franz Josef Land.

Nansen knew well that relying on chronometers for navigation made him vulnerable to such a failure, but he had little practical alternative. Today, anyone with a smartphone has a ready source of time and position information. Satellites of the Global Positioning System (GPS) broadcast clock signals across the globe with uncertainties below 100 ns. These time signals carry the information needed for precise navigation: since radio waves travel at the speed of light, approximately 0.3 meters per nanosecond, comparing signals from different satellites allows position to be determined within a few meters. From seismic monitors to drone delivery, GPS has transformed existing technologies and enabled new ones.

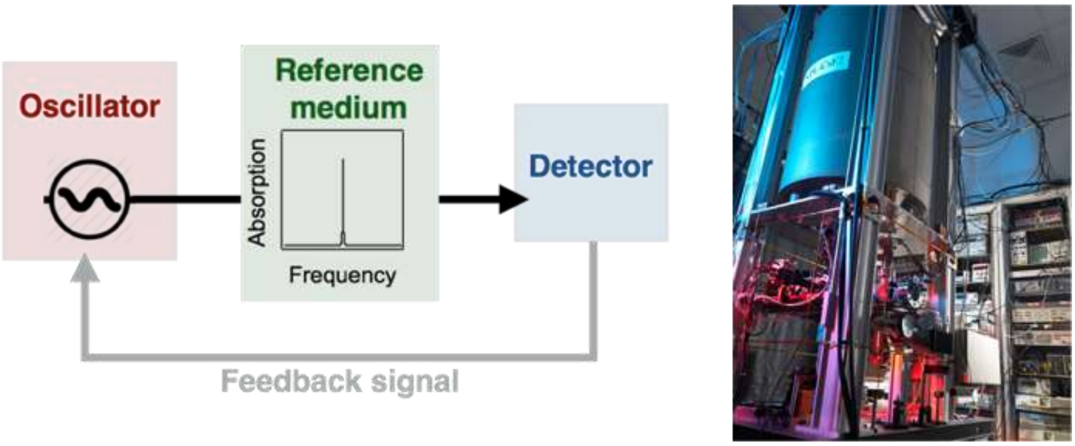


Figure 1 Left: Principle of an atomic clock. The clock signal is generated by a tuneable electrical oscillator. To hold the oscillator at the correct frequency, part of the clock signal is passed through a reference medium such as an atomic vapour. If the oscillator drifts away from the resonance frequency, the change in absorption is detected and a feedback signal is applied. With a reference medium chosen to absorb energy at one precise frequency, the oscillator is stabilised at this value. Right: The CsF2 clock at the National Physical Laboratory, a caesium vapor clock that is the master standard for the United Kingdom..

For all its precision, the GPS signal is not the answer to all timing problems. Central to the system are atomic clocks carried on each satellite. Although these clocks are extremely stable (and regularly calibrated by comparing to national standards laboratories), transferring timing information to the user suffers from many sources of error that, at this extreme precision, introduce significant inaccuracies. But what if we could put this precision directly in the hands of the user? What if we could shrink the atomic clock itself and make it work inside the GPS receiver? Would we, like Nansen, then want to carry our clocks with us?

The core of a present-day atomic clock is a vacuum chamber containing a thin cloud of vaporized metal (usually caesium). Atoms in the vapor resonate at a precise frequency, rather like a pendulum in a grandfather clock. The atomic oscillations, excited using microwave signals and detected with laser light, mark out atomic time (see Figure 1). Unlike pendulums, atoms do not suffer from manufacturing error or wear; with proper isolation from the environment, the frequency is set by the laws of physics. Achieving the necessary level of isolation in practice means that the best atomic clocks take up entire rooms, while commercial atomic clocks are usually the size of suitcases.

In a tour de force of microfabrication, scientists at NIST managed in 2004 to shrink this entire setup into a stack of components a few millimetres high. Such 'chip-scale atomic clocks' are now available commercially, and are used in niche applications such as military communication and underwater navigation. However, this miniaturisation comes at a price, and not just in manufacturing cost: the tiny size of vacuum chamber introduces drift in the clock frequency because of interaction with the chamber walls, while the heater that generates the vapour is a hefty power drain for a portable device. It will be a long time before this technology makes it into your cellphone.

However, there is an alternative, proposed in 2008 by Andrew Briggs and Arzhang Ardavan at Oxford University. Instead of building an atom trap top-down, it makes use of a type of molecule that is nature's own trap: an endohedral fullerene. Endohedral fullerenes (see Figure 2) are remarkable molecules that almost seem to defy ordinary laws of chemical bonding. The outside is a fullerene, a miniature soccer ball of carbon. What makes the molecules special is the contents of this hollow ball: a separate chemical species can be trapped within it without bonding to the shell. Inside the molecule, the encapsulated species is protected from its environment; from the outside, the molecule has similar properties to an empty fullerene.

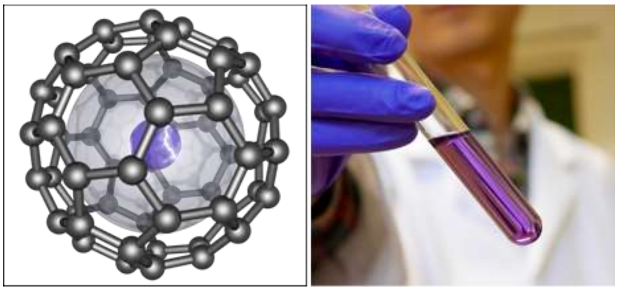


Figure 2 Left: Molecular model of the endohedral fullerene N@C$_{60}$. This molecule is about 0.8 nm across. Right: endohedral fullerenes in solution. A sample like this contains about 0.1 mg of material and costs over \$10,000 to make.

Without doubt the most extraordinary of any endohedral fullerene is N@C$_{60}$ (figure 2). In this case there is very little interaction between the trapped nitrogen atom and the fullerene cage. It is as if the nitrogen atom "floats" inside the fullerene, retaining its atomic characteristics. This is not unique;, noble gas elements such as He, Ne etc. have all been incorporated in C_{60}. However these are very inert species, unlike nitrogen, which is one of the most reactive elements known.

2. N@C_{60}

2.1. Synthesis

N@C_{60} is a molecule that based on the reactivity of nitrogen should not exist. Nevertheless, there are several ways to synthesize N@C_{60}. Extreme conditions are commonly used for all of these methods, because the reaction is thermodynamically unfavourable; it is the chemical equivalent of pushing water uphill.. Once the molecule is formed however, the fullerene cage isolates and stabilizes the nitrogen radical, so the products synthesized can be collected and stored. The ratio of N@C_{60} to C_{60} resulting from different method of synthesis ranges from 1:100000 to 1:100.

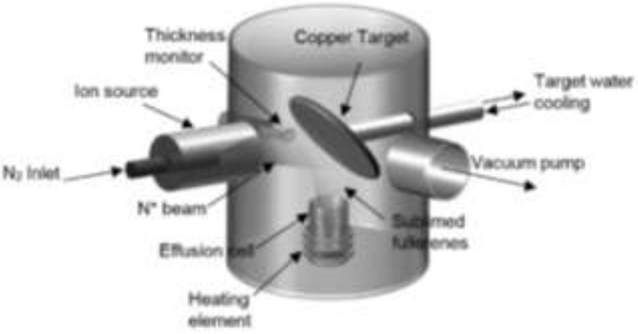
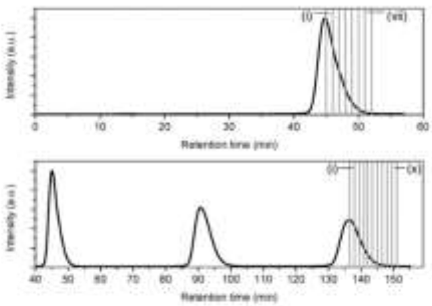


Figure 3 Experimental set-up of a nitrogen implantation apparatus using a commercial ion source.

The most established method is called *ion implantation* using a commercial ion source. Figure 3 illustrates the optimized experiment set-up. An effusion cell is applied to sublime C_{60} and to gradually build up a C_{60} film on a cooled target. The rate of fullerene sublimation is recorded by a thickness monitor, so that a feedback control on the heating power can be applied to obtain a constant deposition rate on the cooling target. While the C_{60} film is growing, nitrogen ions generated by a low-energy, ion source are bombarding the surface of the C_{60} film. Benefiting from the in-situ formation of film and continuous nitrogen bombardment, the productivity of this method is scalable up to grams of crude products per run, while the yield (N@C_{60}/C_{60}) is c.a. 10^{-4} in concentration.



2.2. Purification

Since the synthesis of N@C_{60} offers a mixture of N@C_{60} and C_{60},

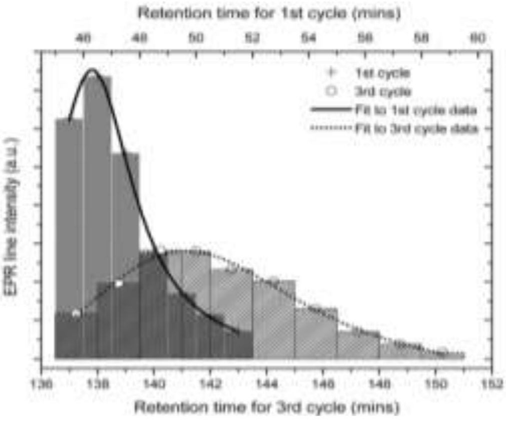


Figure 4 Non-recycling and Recycling HPLC chart for the enrichment of the crude mixture of N@C$_{60}$/C$_{60}$ (top). EPR signal mapping of eluting fractions in different retention times, which reconstructs the eluting curve of N@C$_{60}$ (bottom).

how to separate N@C$_{60}$ from C$_{60}$ is very important. Here lies the problem: C$_{60}$ and N@C$_{60}$ are chemically almost identical. The key word here is *almost*. Small differences in molecular weight and polarizability between the molecules mean that it is possible to separate them by applying a state-of-the-art chromatographic technique called preparative HPLC (High Pressure Liquid Chromatography).

Considering the limited content of N@C$_{60}$ in the crude mixture, the separation is normally performed with multiple stages. At the beginning of the separation, a large quantity of mixture must be processed while the eluting peak of N@C$_{60}$ is not detectable. Conservatively, collecting the second half fraction of C$_{60}$ peak can quickly enrich N@C$_{60}$ in a large scale. When the mixture is enriched to a good extent to resolve the eluting curve of N@C$_{60}$, recycling the mixture enables a complete separation between C$_{60}$ and N@C$_{60}$. Figure 4 shows the typical HPLC purification protocol for N@C$_{60}$. One can see that there is significant overlap between the peaks of C$_{60}$ and N@C$_{60}$, which makes separation fiendishly difficult, but it can be done!

3. Why N@C$_{60}$ is ideal for an atomic clock

Can we exploit this natural trap to make an atomic clock? N@C$_{60}$ is currently our leading candidate. The laws of quantum mechanics prescribe the energy levels available to the atom and set the resonance frequencies at which transitions can occur between them. To act as a good clock reference, we need a resonance that is well-defined in frequency and as stable as possible. This is precisely what this endohedral fullerene offers: most outside influences barely perturb the intrinsically narrow resonance frequency of the encapsulated atom.

The atomic clock scheme works by using the atomic transition, whose frequency is fixed by the laws of physics, to stabilize an electrical oscillator (see Figure 1). To measure the transition, we can exploit the fact that the molecules absorb energy from radio waves if and only if the radio frequency precisely matches the transition frequency. In this scheme, the oscillator generates a radio signal close to the reference transition frequency. This signal is transmitted via an antenna to a cell containing a sample of molecules, either in the form of a powder or dissolved in solution. If the oscillator is correctly tuned, power is absorbed. Conversely, a reduction in the absorbed power shows that the oscillator has drifted away from the molecular transition frequency. Using a feedback mechanism, the oscillator can then be tuned back to the point of maximum absorption. Since the transition frequency in the molecule is precisely known, an accurate time reference follows simply

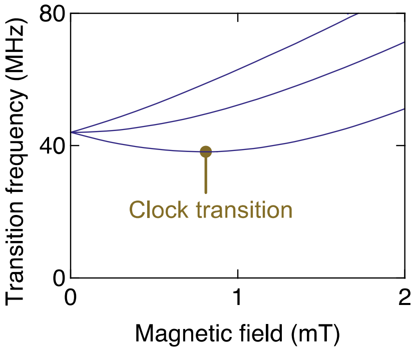


Figure 5 Transition frequencies between quantum levels of the endohedral fullerene N@C$_{60}$, plotted as a function of applied magnetic field. At a magnetic field close to 0.8 mT, the influence of field variations on the lowest transition disappears. At this "clock transition", the frequency stability is optimized.

by counting cycles of the stabilised oscillator.

Endohedral fullerenes such as N@C60 are an outstanding reference material because the transitions between their quantum mechanical spin states have some of the sharpest frequencies ever measured for a molecular species. However, one external influence does penetrate the fullerene cage and perturb the transition frequencies: magnetic fields. Since the world is full of uncontrolled magnetic fields, for example from electric motors, steel vehicles, and the earth itself, protection from them is crucial for a stable clock. What Briggs and Ardavan realised is that for the N@C60 molecule, the energy levels can arrange in such a way as to give a so-called "clock transition"; for this transition, the magnetic influences on the resonance frequency cancel out (Figure 5). To benefit from this clock transition, it is only necessary to apply a small static magnetic field to tune the energy levels close to the point where the errors cancel.

4. Challenges and Opportunities

What motivates us to build such a device is the possibility to incorporate a complete atomic clock into one chip. In this design, the entire operation is based on radio-frequency electronics, avoiding the need for optical elements as used in conventional atomic clocks. Unlike a vapor-based clock, there is no need to maintain a vacuum chamber over years of use, and no power-hungry heater to drain a battery. An endofullerene clock, if it can be built, is thus attractive for the three elements of portability – size, weight, and power consumption. Potentially, it could replace many of the quartz clock chips used in nearly every present-day electronic device.

Historically, every generation of portable timekeepers has led to new possibilities. What might we expect from portable atomic clocks? Early applications are likely to take advantage of the fact that a precise clock is also a precise frequency synthesiser. For example, in wireless communication, multiplexing channels into one frequency band needs every transmitter to keep strictly to its assigned carrier frequency. (This is the reason that some cellphone towers are already equipped with atomic clocks.) As future networks, such as the internet of things, crowd into a limited spectrum, portable and stable clocks will become increasingly necessary.

For a similar reason, GPS receivers will benefit from on-board clocks. This is perhaps surprising, given that the GPS signal itself carries time information, but it happens because the signal from the satellite is weak - comparable to the power of a light-bulb transmitted over an entire continent. Landscape features, buildings, and interference make it harder to detect. To track this weak signal, the receiver must precisely lock to the broadcast frequency. The more stable the local frequency reference, the faster and more reliable this tracking can be.

In hostile environments such as battlefields, this becomes even more important. The GPS signal is vulnerable to jamming, and effective (but illegal) jammers are widely available and likely to be encountered in future wars. With precise timing information, GPS receivers could isolate the true signal above the noise of the jammer. They could even let navigation survive partial destruction of the satellite network; whereas present-day receivers must triangulate their positions from four or more satellites simultaneously, a good enough clock could instead use successive signals from a single satellite. Other defence applications include frequency-hopping communication, bistatic radar (in which an attacker stealthily acquires a radar signal from a target illuminated by a distant transmitter), and sensitive monitoring of enemy communications. For these reasons, portable clocks are of great interest to militaries in several countries.

Finally, there may be completely new applications. For example, warehouses, postal depots, and even subways may in future be equipped with their own local positioning systems using small-scale wireless base stations. Parcels, equipment, and people could then be tracked via time-of-flight of radio signals. Even driverless cars would benefit from an on-board accurate time keeping device especially in challenging terrains, such as tunnels, where satellite GPS signal is weak.

5. Conclusions

For these possibilities to be realised, many elements must come together. First it will be necessary to optimise the stability of the atomic resonance frequency on which the clock depends. To be competitive, the frequency fluctuations must be much less than one part in a million, despite variations of temperature, magnetic field, and chemical environment. Second will be the task of miniaturization – of shrinking sample cell, magnet, and radio-frequency electronics down to a chip-scale device. Third is the need for low power consumption. Last is the need to manufacture endohedral fullerenes on an industrial scale, material that so far exists only in milligram quantities. Despite this, endohedral fullerenes are already starting to appear on the market. Recently a spin-out company from the University of Oxford called Designer Carbon Materials Ltd (www.designercarbon.com) was founded by one of us (Prof. Kyriakos Porfyrakis). The company has begun to sell $N@C_{60}$ and other bespoke endohedral fullerenes to research groups around the world. As applications start to appear, production of these molecules will scale up and price will come down.

The challenges are daunting. For miniaturised atomic clocks to be incorporated on every day devices, many different areas in science and engineering need to be pushed to their limits. But the rewards are fantastically important! We look forward to the day when the hearts of endohedral fullerenes beat time all around us.