Towards a measurement of the nuclear clock transition in $^{229}$Th

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**Abstract.** We investigate a potential candidate for a future optical clock: the nucleus of the isotope $^{229}$Th. Over the past 40 years of research, various experiments have found evidence for the existence of an isomeric state at an energy of a few eV. So far, neither the energy nor the lifetime of the isomer have been determined directly. As the scene is not yet prepared for direct laser excitation, other means of populating the isomer need to be explored. We investigate three different approaches, all of which rely on CaF$_2$ crystals doped with $^{229}$Th or $^{233}$U. Various kinds of crystal luminescence are discussed in detail.

1. The few-eV isomer in $^{229}$Th

Any scientific clock is evaluated along two dimensions: its accuracy to tell the time, and its (in)sensitivity to external perturbations. A promising new platform that could “host” a clock that excels in both aspects is the nucleus of an atom or ion. The system would be intrinsically very small (typical size 5 fm) and could benefit from shielding from environmental effects by the electron cloud. Using the relations $\Delta x \cdot \Delta p > \hbar$ and $E = p^2/2m_p$, the length scale of 5 fm can be related to an energy scale of about 1 MeV. Nuclear decay energies are indeed on the MeV scale, and typical energy differences between adjacent nuclear states are between a few 10 keV and a few 100 keV. Unfortunately, coherent narrow-line X-ray sources, capable of driving such nuclear transitions, are not yet available. To date, the nuclear clock remains a vision.

There is, however, a very special case encountered in $^{229}$Th (a freak of nature, if you like): this isotope possesses an extremely low-lying state with an excitation energy of only a few eV. According to Fermi’s Golden Rule, the lifetime of this state scales as $E^{-3}$ for an M1 transition into the ground state, such that its expected lifetime is comparably large: about an hour. This setting of (i) a transition that can be reached with existing laser technology, (ii) an extremely narrow linewidth, and (iii) a nuclear system well-protected from external perturbation, makes $^{229}$Th a promising candidate for a future nuclear optical clock [1]. Being able to control and manipulate a nuclear system with a laser light, even transferring the well-established toolbox of optical spectroscopy to a nuclear system, is an exciting prospect. In addition, nuclear transitions might be highly sensitive to drifts in fundamental constants. Not surprisingly, this laser-driven nuclear two-level system has been proposed for a number of quantum optics applications, among
them a gamma-ray laser. A recent review of E. Peik and M. Okhapkin [2] gives a full account of the current work in this field of research.

Unfortunately, the energy of the isomer is not yet known precisely enough to commence direct laser spectroscopy; the most recent gamma spectroscopy measurement places the energy at 7.8(5) eV, corresponding to a wavelength of 160(10) nm [3]. Key parameters are given in Fig. 1(a). Besides the radiative de-excitation of the isomer, internal conversion (IC) and related processes have been discussed. Indeed, the “demon” of non-radiative decay might preclude fluorescence detection schemes whenever the isomer is given the possibility to decay through coupling to electronic states. The first ionization energy in thorium is below the expected isomer energy, so the $^{229}$Th atom needs to be in an ionized state.

There are currently two main platforms envisioned for a future optical clock: crystals and ion traps [1, 2]. Ions traps would offer full control over all quantum degrees of freedom and thus enable high-precision spectroscopy, potentially exploiting the full line-$Q$ of $\Delta E/E \approx 10^{-19}$. As a downside, ion traps can load only a limited number of Th ions (typically between 1 and $10^6$). Doped crystals, on the other hand, would enable optical Mössbauer spectroscopy on an ensemble of $10^{15}$ or more ions. Such crystals form a very secure, robust, room-temperature platform with an obvious potential for small-scale integration. Spectroscopy, however, would suffer from effects related to the crystal structure, such as fast decoherence (of order kHz), line shifts (GHz scale), broadening (kHz widths), and crystal luminescence. One might argue that crystals might be useful for the initial search for the transition and future solid-state applications (e.g. for clocks on satellites), whereas ion traps will provide the ultimate quantum control and most precise measurements.

The Vienna group follows the solid state approach and has placed its bets on CaF$_2$ [4]. Crystals of 17 mm diameter and 40 mm length are routinely produced in our in-house crystal-growing apparatus. We employ the vertical gradient freeze method, which ensures a homogeneous distribution of the dopant over the crystal volume. CaF$_2$ readily accepts Th and U as dopants, and concentrations of up to 1% have been achieved. Our $^{229}$Th:CaF$_2$ crystals have a relative concentration of a few $10^{-7}$, limited by the available quantity of $^{229}$Th. The crystals are cut and polished to discs. Transmission in the UV is found to be slightly smaller compared to commercial crystals, but the transmission through a 1-cm crystal is still well over 50% at 160 nm; see Fig. 1(c).

Figure 1. (a) Key parameters of the nuclear clock transition in $^{229}$Th. (b) The CaF$_2$ lattice structure, with a Th$^{4+}$ ion replacing a Ca$^{2+}$ ion. The additional charges are compensated by two fluorine interstitials. (c) Transmission of crystals in the UV range. The grey line shows the transmission of a 5-mm home-grown pure CaF$_2$ crystal, which is not altered by Th doping concentrations of up to $10^{-5}$. The black line is a 4-mm U:CaF$_2$ crystal at $5 \times 10^{-5}$ doping concentration.
Figure 2. Light-induced luminescence in CaF$_2$. (a) The famous self-trapped exciton (STE) spectrum of CaF$_2$, consisting of individual lines. The signal below 240 nm is magnified by a factor of 1000 to show the absence of luminescence. (b) The same lines appear in the thermoluminescence spectrum, however at different relative amplitudes. (c) Zoom into the STE spectrum, with multiple Gaussian peaks fitted to the data. Converting to peak positions into units of energy (inset) reveals an almost equidistant spacing.

2. Luminescence of CaF$_2$ crystals

The crystal luminescence could potentially mask the isomer signal if it appears in the same spectral range (around 160 nm) and has a similar decay time (of order 1000 s). Unfortunately, the rare-earth halides (e.g. CaF$_2$) are well known for their scintillation properties. Luminescence can be induced by various means, such as UV light, X-rays, and dislocations caused by the passage of massive particles following radioactive decay.

2.1. Photoluminescence

To assess the photoluminescence spectrum, we illuminate home-grown crystals with VUV light derived from a deuterium lamp. The excitation is turned off, and the luminescence spectrum emitted by the crystal is measured with a spectrometer; see Fig. 2(a). The dominant spectral feature is the signature of the well-known self-trapped exciton (STE) structure, consisting of multiple states in a near-harmonic oscillator potential (Fig. 2(c)). The amplitude of the individual lines changes slightly with experimental parameters, but no emission is observed at wavelengths below 260 nm. This is very promising, as the primary search range for the isomer transition is around 160 nm.

Note that STEs are a generic feature of CaF$_2$: primary crystal defects, as induced by UV light, quickly thermalize into comparably long-lived excitations, such as STEs. These may decay through radiation of a photon. The susceptibility to form short-lived primary defects depends on the “cleanliness” of the crystal. Our home-grown undoped CaF$_2$ crystals show $10^4$ times more photoluminescence compared to commercial crystals. The photoluminescence is not caused, changed, or enhanced by the doping.

Very long-lived defects can be annealed by heating the crystal to a few 100°C, such defects also relax via STEs; see Fig. 2(b). The same emission spectrum is recorded in response to 30-keV X-ray illumination. Detailed studies concerning the time-dependence and temperature dependence of photoluminescence can be found in Ref. [5].
Figure 3. Radioluminescence of CaF$_2$, (a) induced by 5 kBq of $^{229}$Th doped into the crystal (resolution 15 nm), and (b) induced by 7.5 MBq of $^{233}$U in proximity to the crystal (resolution 4 nm). The grey line shows the STE-spectrum as a reference. Note the Cherenkov radiation between 120 and 200 nm in panel (b).

2.2. Radioluminescence: alpha decay
We record the emission spectrum of $^{229}$Th-doped crystals, where the alpha decay of $^{229}$Th (lifetime 7932 years) leads to scintillation. The activity of 5 kBq induces only a small signal (Fig. 3(a)), but we can already see that the emission has an abrupt UV cut-off at 220 nm. This feature is a property of CaF$_2$ and does not depend on doping, defects, impurities, and the like. The emission spectrum looks very different for other types of crystals, e.g. MgF$_2$, and it is strikingly different from photoluminescence. Further investigations can be found in Ref. [5].

To increase the signal strength, we bring a 7.5 MBq sheet of $^{233}$U in physical contact with a commercial CaF$_2$ specimen; see Fig. 3(b). The large signal allows us to resolve the substructure of the spectrum. By placing different absorber materials between the source and the crystal, we are able to show that at least 90 % of the emission between 220 and 400 nm is caused by alpha particles.

2.3. Radioluminescence: beta decay
While the lifetime of $^{229}$Th is comparably long, all of its daughters along the chain down to the stable $^{209}$Bi are short-lived. These decays (5 alpha and 3 beta) contribute to the radioluminescence. The spectral signature of beta decays is very different from the one of alpha decays: electrons above a threshold of 160 keV kinetic energy generate Cherenkov radiation, predominantly at UV wavelengths; see Fig. 3(b). This emission is intrinsically broadband and very “flat”, thus is poses a locally homogeneous background for the sought-after narrow-linewidth isomer signal. As all relevant properties of the decay chain are known, the spectrum and absolute amplitude of the Cherenkov radiation can be calculated. High-energy gammas can also generate high-energy electrons through Compton scattering, but this mechanism adds only a minor contribution to the Cherenkov emission.

3. Three experimental approaches to populate the isomer
We will now present three different experiments of our group, ongoing or planned for the near future. All of them rely on doped crystals, but follow very different approaches to populate the isomer. The three schemes are sketched in Fig. 4; different crystals are required for each approach. In all experiments, the VUV gamma emitted during de-excitation of the isomer is measured with a UV spectrometer. Unfortunately, none of these approaches is immune to parasitic non-radiative decay via IC or related processes.
3.1. Direct spectroscopy using synchrotron radiation

Direct spectroscopy of $^{229}$Th:CaF$_2$ crystals with a doping concentration $3 \times 10^{-7}$ (corresponding to $7 \times 10^{15}$ cm$^{-3}$ in density) will be performed at the MLS synchrotron facility in Berlin. The synchrotron radiation (linewidth about 5 nm, flux about 100 photons/(s × Hz)) can be scanned across the entire search range. Preliminary measurements will be performed with a Cs-Te PMT detector, such that photoluminescence will constitute the main background. Once a signal is detected, either a monochromator in the beamline or a spectrometer can be employed to improve the uncertainty of the wavelength to below 0.1 nm. Two very similar experiments performed recently were unable to find evidence of the isomer emission [6, 7], possibly due to competing non-radiative decay channels.

We expect Cherenkov radiation (induced by radioactive decay of $^{229}$Th) to be the main source of background emission below 200 nm. The amplitude and spectrum of Cherenkov radiation can be calculated exactly [8]. We estimate that, for the specific parameters of our experiment and negligible non-radiative decay, the isomer signal should rise above the noise of the Cherenkov background after less than an hour of illumination/detection cycles.

3.2. A nuclear lambda-system using the 29-keV state

Direct excitation with synchrotron radiation in the UV range is complicated by the fact that neither energy nor lifetime of the isomer are known, requiring a two-dimensional search. To circumvent these uncertainties, the isomer can be populated through pumping via the second excited state in the $^{229}$Th nucleus; see Fig. 4(b). The energy of this state (29,185.6(2) eV) is known to within the linewidth of the excitation X-ray source, and its lifetime is 200(50) ps. Established detector technologies using fast MCPs allow to detect the re-emitted, delayed 29-keV gamma, proving that the excitation is on resonance and that the isomer is indeed populated. Spectral resolution of the isomer emission is obtained with a spectrometer. Test measurements at SPring-8 have shown that the search range around 160 nm is free of crystal luminescence caused by the excitation X-ray. Mildly doped CaF$_2$ can stand X-ray illumination for hours.

For experiments using UV excitation, we chose CaF$_2$ as the crystal material for its optical properties. For the X-ray excitation, choice of the material is guided by its X-ray properties (attenuation and hardness). Given that the mass attenuation increases heavily with mass number, it is desirable to work with crystals composed of lighter atoms. Changing from CaF$_2$ to MgF$_2$ already increases the penetration length at 29 keV from 1.3 to 4.7 mm.

Apart from a measurement of the isomer energy and its lifetime, this approach contains all the ingredients of an (admittedly very inefficient) gamma-ray laser: for strong enough pumping, an inversion between ground and isomeric state can be achieved, potentially leading to lasing on the nuclear transition.

Figure 4. Three approaches to populate the isomer: (a) direct excitation on the nuclear clock transition using synchrotron radiation, (b) optical pumping via the 29-keV state, (c) alpha decay of $^{233}$U with a 2% branching ratio into the isomer.
This line of experiments is performed in close collaboration with the group of K. Yoshimura at Okayama University, and experiments are performed at the SPring-8 facility.

3.3. Uranium-doped crystals
A large number of past and presently ongoing experiments use the alpha decay of $^{233}$U into $^{229}$Th as a means to feed the isomer state (branching ratio about 2%). Most experiments are designed such that a thin layer of $^{233}$U is brought near a UV-transparent medium (usually MgF$_2$). Upon an alpha decay, the $^{229}$Th obtains a recoil of up to 84 keV, which allows it to penetrate through the thin $^{233}$U layer and deposit onto, or penetrate a few 10 nm into, the crystal. The crystal is then placed into the detector. The main advantage of this approach is the fact that the massive energy released in the alpha decay is separated in both space and time from the isomer detection. We have shown, however, that crystal luminescence caused by alpha decay is spectrally remote from the isomer search region. Equally important, the radioluminescence that does overlap with the expected isomer wavelength (beta radiation from ingrowth of daughters) is fully captured by the detector. Given that the signal rate is intrinsically low (given by the 160 000 years lifetime of $^{233}$U and the 15 nm path length through the uranium), it is desirable to increase the signal strength.

We could show that doping $^{233}$U directly into suitable crystals has the potential to increase the signal rate by at least two orders of magnitude at the very same S/N as with surface-implantation experiments. The fundamental limitation with uranium-doped crystals stems from the absorption of uranium in the UV range. We have measured the transmission properties of $^{238}$U-doped crystals (Fig. 1(c)) and found that the maximum flux of isomer gammas emitted from such a crystal is about 4000/(cm$^2 \times s$), giving reason for hope that emission on the isomer transition can be detected. The main signal background is caused by beta decay of daughters in the $^{233}$U chain, which is an unavoidable contamination in the $^{233}$U source. Assuming the absence of IC processes and using parameters of a standard UV spectrometer, we calculate that the isomer signal should rise above the noise of the Cherenkov emission for measurement times of a few hours.

4. Conclusion
We have described three experiments, planned or ongoing, to measure the wavelength of the $^{229}$Th isomer transition. The experiments use very different means to excite the isomer. All of these experiments are sensitive to a background of Cherenkov radiation in the VUV regime [8], and all of them require the radiative de-excitation channel to be of at least a few percent compared to competing non-radiative channels.

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