Comment on “Prospect of optical frequency standard based on a \( ^{43}\text{Ca}^{+} \) ion”

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A recent evaluation of the frequency uncertainty expected for an optical frequency standard based on a single trapped \( ^{43}\text{Ca}^{+} \) ion was published in Phys. Rev. A 72 (2005) 043404. The paper contains some interesting information like systematic frequency shifts but fails to depict their uncertainty, leading to confuse accuracy and precision. The conclusions about the major contribution to the frequency shift are not consistent with the presented calculations and omit comparisons with data published previously.

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Optical frequency standards based on single trapped ions may reach ultimate performances which are orders of magnitude better than the existing cesium clocks in the microwave domain \cite{1}. A recent evaluation of residual effects in a frequency standard based on a single \( ^{43}\text{Ca}^{+} \) ion predicts an ultimate attainable precision below \( 10^{-15} \) \cite{2}. This evaluation takes into account shifts due to local fields neglecting their uncertainty. In this comment we show that a more complete and precise analysis of the residual field effects is necessary to predict the potential frequency uncertainty \cite{3}.

The proposal of a single \( ^{43}\text{Ca}^{+} \) ion stored in an rf trap as an optical frequency standard is based on its ultranarrow \((\Delta \nu_{\text{nat}} < 160 \text{ mHz})\) electrical quadrupole clock transition at \( 4.1 \times 10^{14} \text{ Hz} \) and its relatively simple energy level scheme with all wavelengths in the optical domain, allowing the concept of an all solid-state laser set-up (cf. figure \ref{fig:level_scheme}).

The advantage of using the very rare \((0.135\% \text{ of natural abundance})\) odd isotope \( ^{43}\text{Ca}^{+} \) compared to the most abundant \( ^{40}\text{Ca}^{+} \) relies in the possibility of eliminating the first order Zeeman shift by using a \( m = 0 \) sublevel, while the second order Zeeman shift is minimized by the choice for the clock transition of the hyperfine levels \( |4S_{1/2}, F = 4\rangle \) and \( |3D_{5/2}, F = 6\rangle \) \cite{2,3}. Although the value of the magnetic field and its fluctuations remain an important issue as this may be one of the major causes of uncertainty in the frequency shifts, the evaluation of this uncertainty is not addressed in \cite{2}. A minimum magnetic field is indeed required to split the chosen transition from the two closest ones \( |4S_{1/2}, F = 4\rangle \rightarrow |3D_{5/2}, F = 6, \pm 1\rangle \), however the choice made in \cite{2} of a \( 0.2 \mu T \) (2 mG) magnetic field is not motivated and the expected fluctuations of such a field are not given. Magnetic field fluctuations as big as \( 0.2 \mu T \) over one day have been observed in an unshielded environment \cite{4}. Then, exploiting the linear Zeeman shift of the \( |4S_{1/2}, F = 4\rangle \rightarrow |3D_{5/2}, F = 6, \pm 2\rangle \) transitions like suggested in \cite{2} may not be sufficient to correct these fluctuations over one day. As the Zeeman effect is quadratic, its fluctuations depend linearly on the strength of the magnetic field and on the amplitude of its fluctuations. With a \( 0.2 \mu T \) magnetic field and \( 0.2 \mu T \) fluctuations, the Zeeman frequency shift uncertainty is twice the Zeeman shift itself and reaches 0.72 Hz. In fact, the choice of the magnetic field results from a compromise between maintaining a high level of fluorescence \cite{5}, splitting the sublevel transitions and keeping the Zeeman effect fluctuations low. A complete description of the magnetic field (average value and fluctuations) is therefore needed to estimate the uncertainty induced by the Zeeman effect, which is missing in \cite{2}.

The other significant effect causing frequency shift is the Stark effect. It can be evaluated through the polarizability of the states involved in the clock transition. The calculation presented in \cite{2} is however only partial. On the one hand, the anisotropic contribution (tensorial part) of the \( D_{5/2} \) polarizability is not mentioned. This

\[\begin{align*}
\text{FIG. 1: Lower energy levels of the } ^{43}\text{Ca}^{+} \text{ ion. All wavelengths required for laser-cooling and interrogation of the ion can be generated by solid-state lasers.}
\end{align*}\]

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The effect of the electric quadrupole moment of the \(3D\) state to any electric field gradient, its contribution to the uncertainty can be reduced to the 0.1 Hz level \(2\) \(3\) by measuring the transition frequency for three orthogonal directions of the magnetic field, like first proposed in \(7\).

In a thorough investigation of line-broadening effects, the AC Stark (or light) shift depending on the laser intensity used to probe the clock transition at 729 nm should also be evaluated. Actually, for a Rabi frequency of 1000 \(s^{-1}\) and a detuning smaller than \(\pm 10\) Hz to probe the low- and the high-frequency side of the clock transition, the effect may be as small as \(\pm 6\) mHz for a magnetic field of 0.1 \(\mu T\) \(2\).

In summary, the overall uncertainty budget given in \(2\) is not complete. First, the most significant frequency shift does not come from the quadratic Zeeman effect since the static Stark effect is as big as this last effect (0.40 Hz compared to -0.36 Hz). Second, the uncertainty of the frequency shifts must be evaluated to estimate the precision of the clock \(1\), which is missing in \(2\). In our previous paper \(3\), we conclude that, if at 300 K, the major source of relative frequency uncertainty (\(\pm 9 \times 10^{-16}\)) would be due to the Stark effect, for a vessel cooled down to 77 K, the uncertainty would result from the fluctuations of the quadratic Zeeman effect and from the experimental uncertainty in pointing three orthogonal directions for compensating the quadrupole shift. It was estimated to \(\pm 4 \times 10^{-16}\) (relative uncertainty) with room for improvement. All the contributions to the systematic frequency shift and its uncertainty are summarized in table \(\text{I}\) which is reproduced from reference \(3\).

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**TABLE I: Uncertainty budget for the frequency transition of \(|S_{1/2}, 4, 0\rangle \rightarrow |D_{5/2}, 6, 0\rangle\) in \(^{43}\text{Ca}^+\)**

| effect | fields/conditions | shift (Hz) @ 300 K | @ 77 K |
|--------|-------------------|--------------------|--------|
| second order Zeeman effect | 0.1 \(\mu T\) Stark effect | radiated and bias static field | +0.09 ± 0.09 | -0.09 ± 0.09 |
| \(D_{5/2}\) coupled to the field gradient | 1 V/mm\(^2\) | +0.39 ± 0.27 | -0.36 ± 0.36 |
| AC Stark effect @ 729 nm | 0.75 \(\mu W/mm^2\), 0.1 \(\mu T\) second order Doppler effect | ion cooled to the Doppler limit | \(+0.006\) | \(+0.006\) |
| global shift and uncertainty | 10 Hz to probe the clock transition | \(-1 \times 10^{-4}\) | \(-1 \times 10^{-4}\) |
| relative shift and uncertainty | ion cooled to the Doppler limit | \(+7(\pm 9) \times 10^{-10}\) | \(-2(\pm 4) \times 10^{-10}\) |

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