Simplest Molecules as Candidates for Precise Optical Clocks

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The precise measurement of transition frequencies in cold, trapped molecules has applications in fundamental physics, and extremely high accuracies are desirable. We determine suitable candidates by considering the simplest molecules with a single electron, for which the external-field shift corrections can be calculated theoretically with high precision. Our calculations show that H_2^+ exhibits particular transitions whose fractional systematic uncertainties may be reduced to 5×10^{-17} at room temperature. We also generalize the method of composite frequencies, introducing tailored linear combinations of individual transition frequencies that are free of the major systematic shifts, independent of the strength of the external perturbing fields. By applying this technique, the uncertainty of the composite frequency is reduced compared to what is achievable with a single transition, e.g., to the 10^{-18} range for HD^+. Thus, these molecules are of metrological relevance for future studies.

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Frequency metrology of cold trapped molecules is an emerging field, driven by the promise of opening up new opportunities in fundamental physics. It has been proposed to use these systems to test the constancy of fundamental mass ratios (m_e/m_p, m_p/m_d), by measuring vibrational transition frequencies over time [1]. The comparison of experimental molecular transition frequencies with theoretical results can test *ab initio* calculations, in particular QED effects [2,3], can determine mass ratios of small nuclei, and can set limits to a "fifth force" on the subnanometer scale [4]. The search for parity and Lorentz invariance violation effects on vibrational frequencies also requires extreme frequency accuracy [5,6]. Different molecular systems are therefore being investigated [7–10].

Tests of the constancy of m_e/m_p using microwave cold atom clocks (exhibiting 2×10^{-16} fractional uncertainty) are already producing stringent limits. For molecules to become competitive systems, they must reach an uncertainty in the 10^{-17} range. A crucial aspect in molecular frequency metrology is thus the understanding of systematic frequency shifts of their transitions, the development of methods allowing their suppression or, at least, their quantification, and the identification of candidate systems [11–16].

In this Letter, we discuss and answer affirmatively the question whether it is in principle possible to reach extremely low inaccuracies (10^{-18} range). We propose the *simplest* molecules, i.e., molecules with one electron, for which the *ab initio* theory has made significant advances in the last decade [17]. It allows the calculation of transition frequencies with fractional inaccuracies of, currently, 4×10^{-11} [18], and, crucially, also the accurate calculation of their sensitivity to external perturbing fields [19].

The composite frequency method and simple molecules.—A significant difference between atoms and molecules is that molecules have a multitude (many tens) of long-lived rovibrational levels in their electronic ground state, each of which may have a substantial number of hyperfine states. Thus, there is also a very large number (thousands) of transitions having high spectroscopic quality factors. Their external-field shift coefficients $\Delta\eta_j$ vary, often substantially, because the states' rovibrational molecular wave functions vary, and in consequence the coefficients of the hyperfine Hamiltonian also vary. A subset of these transitions may exhibit particularly small $\Delta\eta_j$. The computability of the external-field shifts of simple molecules then has two main consequences. First, it permits selecting from the large set of transitions the metrologically most advantageous ones based *entirely on theory*. Second, the computability also enables a new approach for a reduction of the systematic shifts, which is particularly direct in molecules. Here, one performs, in fairly rapid succession, measurements of a set of N selected transitions with frequencies $\{f_1, f_2, ..., f_N\}$ under time-independent and moderate, but otherwise arbitrary, external perturbations $\{X_j\}$, and numerically combines the results with predetermined weights β_i to a composite transition frequency $f_c = \sum_{i=1}^{N} \beta_i f_i$. For the studies mentioned above, such a composite frequency is as useful an observable as the frequency f_i of an individual transition.

Consider now that each individual frequency f_i is perturbed by the external fields present (magnetic field, electric field, electric field gradients, temperature, laser intensities, etc.) in a way expressible as a power series,

$f_i(\{X_j\}) = f_{0,i} + \sum_j \Delta\eta_{j,i}(X_j)^{n_j}$, where $f_{0,i}$ are the unperturbed frequencies, and $\Delta\eta_{j,i}$ are the sensitivities to the various external fields, precisely calculable *ab initio*. Only those contributions that are relevant for a desired accuracy of the composite frequency are included in the expansion, and the possible occurrence of different powers n_j for the same field X_j may also be taken into account.

The weights β_i are computed from the conditions that the sensitivities of the composite frequency to the external perturbations (up to the orders described by the above power expansion) vanish,

$$\partial f_c/\partial(X_j^{n_j}) = \sum_{i=1}^{N} \beta_i \Delta\eta_{j,i} = 0. \tag{1}$$

If M is the number of systematic effects to be canceled, including different algebraic dependencies on the perturbation strengths, there are M such equations, and one needs to measure at least $N = M + 1$ transitions, possibly having significantly different frequencies, to satisfy them. Thus, the β_i are found by solving this set of equations. We stress that the β_i are functions of the theoretical shift coefficients $\Delta\eta_{j,i}$, but are independent of the external fields.

At a simpler level, composite frequencies are determined in atomic clocks in order to suppress the linear Zeeman shift [20]. A composite frequency concept allowing the cancellation of the blackbody radiation shift in atomic clocks using atoms allowing for two clock transitions has been proposed [21].

Here we illustrate this concept for the one-electron molecules $H_2{}^+$ and HD^+. Conceptually, we envision the spectroscopy of these ions to be performed on a single molecular ion, trapped in an ion trap. It is both sympathetically cooled to the Lamb-Dicke confinement regime, and interrogated by a laser-cooled atomic ion (Be^+) using a quantum-logic-type [22] or optical-force detection [23]. Techniques of quantum-state preparation are applied [3,24,25]. We consider here only one-photon transitions, which avoid the relatively large light shifts associated with the large intensities of the spectroscopy laser in two-photon transitions [16,26]. In HD^+ the one-photon transitions are electric dipole ($E1$) transitions with quality factors of order 10^{13}; in $H_2{}^+$ one has to resort to electric quadrupole ($E2$) transitions, since there are no allowed $E1$ transitions in the ground electronic state. Such transitions have been considered theoretically (without hyperfine structure effects) in Refs. [27–29]. Since the lifetime of all $H_2{}^+$ levels exceeds 10^6 s, the transition quality factor will in practice be determined by the laser line width or the interrogation time. An $E2$ transition in a trapped and cooled molecular ion has recently been observed [30].

Theoretical methods—.The main external field shifts relevant for a trapped molecular ion are the Zeeman shift, the Stark and electric quadrupole (EQ) shift caused by the electric field of the ion trap, the black-body radiation (BBR) shift, light shifts and the second-order Doppler shift. In this work, we treat explicitly the first four shifts. For $H_2{}^+$, Karr computed the light shifts of $E2$ transitions and showed that for the fundamental transition $v = 0 \to v' = 1$ (v, v' are the vibrational quantum numbers) they can be reduced to a negligible level [31]. This can also be achieved for light shifts for $E1$ transitions in HD^+. The second-order Doppler shift scales inversely with the mass and thus will be significantly larger than in atomic ion clocks, at the fractional level 10^{-16}, and its uncertainty is therefore a relevant issue. While a discussion of the projected experimental level is beyond the scope of this work, nevertheless a value in the 10^{-18} range might be achievable.

We compute the systematic shifts using highly accurate nonadiabatic, variational wave functions [32]. Because the hyperfine splitting and Zeeman shift typically dominate the other shifts, we first compute the eigenstates $|m(B)\rangle$ of the Hamiltonian $H_{\mathrm{eff}}^{\mathrm{hfs}}(v,L) + V^{\mathrm{mag}}(v,L)$ [13,33–35]. The states m are labeled with S, the quantum number of the total spin, J, the total angular momentum, J_z, the projection on to the z axis parallel to the magnetic field $\mathbf{B}$, and, for $H_2{}^+$, I, the quantum number of the total nuclear spin, or, for HD^+, F, the quantum number of the electron-proton coupled spin. For the Zeeman shift $f_Z(m(B))$, it is sufficient to consider the terms of lowest-order in B, $f_Z(m) \simeq f_{Z1}(m) + f_{Z2}(m) = \eta_B(m)B + \eta_{B^2}(m)B^2$ [13,15]. For each eigenstate, we then compute the expectation value of the (EQ) and dc Stark (S) effective interaction Hamiltonian, $V^{\mathrm{EQ}}(v,L) + V^S(v,L)$, for given strengths of the additional external fields $X_j = V_{zz}, E_t, E_z$, where E_t (E_z) is the electric field component orthogonal (parallel) to $\mathbf{B}$ and $V_{zz} = -\partial E_z/\partial z$. V^{EQ} and V^S have been derived in [16,36] and only the results are given here. The EQ shift is, to a good approximation, $f_{\mathrm{EQ}}(m) = \eta_{Vzz}(m)V_{zz} = (3/2)^{3/2}E_{14}(v,L)V_{zz}\langle m(B)|L_z^2 - \mathbf{L}^2/3|m(B)\rangle$, where the quadrupole coefficients $E_{14}(v,L)$ have been computed in the Born-Oppenheimer approximation. The latter limits the fractional accuracy to $\simeq 10^{-3}$. The Stark shift is $hf_S(m) = -[\alpha^{(t)}(m(B))(E_x^2 + E_y^2) + \alpha^{(l)}(m(B))E_z^2]/2$, where the transverse and longitudinal static polarizabilities are computed as $\alpha^{(t,l)}(m(B)) = \alpha_s(v,L) + \gamma^{(t,l)}\alpha_t(v,L)\langle m(B)|L_z^2 - \mathbf{L}^2/3|m(B)\rangle$, with $\gamma^{(l)} = 2$, $\gamma^{(t)} = -1$. We have computed the scalar $[\alpha_s(v,L)]$ and tensor $[\alpha_t(v,L)]$ polarizabilities nonadiabatically, using the nonrelativistic variational wave functions [36]. The inaccuracies of the polarizabilities are of order 10^{-4} due to the neglect of relativistic effects (of relative order α^2) [37].

The BBR shift of a transition, Δf_{BB}, is determined by the dynamic scalar polarizabilities $\alpha_s(\omega)$ of initial and final states, in case of an isotropic and unpolarized BBR field. The shift is to a very good approximation independent of the hyperfine state and only depends on the initial and final rovibrational levels (v,L), (v',L'). Using our computed polarizabilities and accurate transition dipoles of Ref. [38], we computed the BBR shifts and their temperature derivatives for both HD^+, extending the results of Ref. [14], and $H_2{}^+$. For the homonuclear ion $H_2{}^+$ the shift can be approximately obtained from the static scalar polarizability $\alpha_s(v, L,)$ only, $\Delta f_{BB}(T_0) \simeq \Delta\eta_T T_0^4 = -(832\,\mathrm{V/m})^2(T_0/300\,\mathrm{K})^4 \Delta\alpha_s/2h$, where T_0 is the temperature of the BBR radiation field, and $\Delta\alpha_s = \alpha_s(v', L') - \alpha_s(v, L)$. We also computed the correction of the shifts due to the frequency dependence of the contribution of the excited electronic levels to the polarizability [36]. For H_2^+ we find that the static approximation is sufficient, and thus the fractional inaccuracy of the BBR shift coefficients is $\sigma_{y,\Delta\eta_T} = 1 \times 10^{-3}$. For HD^+, when taking into account all dynamic effects and in the nonrelativistic approximation, we reach a theoretical uncertainty of $\Delta f_{BB}(T_0)$ as low as $\sigma_{\mathrm{abs},\Delta f_{BB}} = 0.03$ mHz. Here, we conservatively assume $\sigma_{\mathrm{abs},\Delta f_{BB}} = 0.1$ mHz.

Systematic shifts of the molecular ions.—We have performed the analysis of the systematic shifts of $H_2{}^+$ searching for metrologically advantageous transitions by first applying the criterion of particularly small Zeeman shifts. For experimental reasons we consider only transitions originating in the vibrational ground state $v = 0$ and we limit the final states to those for which $v' \leq 4$. We also note that the $E2$ transition strengths decrease rapidly with increasing $|v' - v|$ [27] and therefore small values are experimentally favorable. $E2$ transitions with small linear Zeeman shifts are mainly those between the particular homologous hyperfine states, $(v, L, I, S = I + 1/2, J, J_z) \rightarrow (v', L' = L, I' = I, S' = S, J' = J, J'_z = J_z)$. Among these are of interest transitions between states with (i) $J = S + L$, $J_z = \pm J$ (stretched states), (ii) L even, $I = 0, S = 1/2$, $J = L - 1/2$ or $J = L + 1/2$, various J_z, (iii) $L = 3$, $I = 1, S = 3/2, J = 3/2$ or $J = 9/2$, various J_z.

Their small linear Zeeman shift coefficient $\Delta\eta_B$ is a result of the near cancellation of the shift coefficients η_B of lower and upper state, which lie in the range $|\eta_B| \simeq (0.15 - 1.5)$ MHz/G [34]. Importantly, the average linear Zeeman shift of the transition pair $J_z \rightarrow J_z{}' = J_z$ and $-J_z \rightarrow J_z{}' = -J_z$ vanishes. The quadratic Zeeman shift coefficient $\Delta\eta_{B^2}$ is zero in case (i), and small for cases (ii) and (iii). Furthermore, for (ii) the average quadratic shift of the transition between the homologous states $J_1 = J_1{}' = L - 1/2, J_{z,1} = J_{z,1}{}'$ and the transition between states $J_2 = J_2{}' = L + 1/2, J_{z,2} = J_{z,2}{}' = J_{z,1}$ vanishes. A list of favorable transitions, including some that are not of the above type, is given in the Supplemental Material, Table I, [39].

The spectroscopy of a single transition can already reach a high accuracy, for well-chosen transitions. We assume realistic experimental conditions and performance (Supplemental Material, Sec. A [39]). One technique for reducing the EQ shift consists in measuring the transition frequency as the average of three values obtained with the quantization axis (magnetic field) oriented in three orthogonal directions [16]. The quadratic Zeeman shift can be corrected for by measuring the Zeeman pair $J_z \rightarrow J_z{}' = J_z$ and $-J_z \rightarrow J_z{}' = -J_z$ and using the frequency difference to determine the magnetic field strength. For $H_2{}^+$, consider the two Zeeman components of the transition between the homologous states $(I = 0, S = 1/2, J = 7/2, J_z = \pm 5/2)$ [case (ii)] of $(v = 0, L = 4) \rightarrow (v' = 1, L' = 4)$, which have a particularly small EQ shift (see the Supplemental Material, Table I [39]). Assuming that the orthogonal direction technique permits compensation of the individual EQ shift to a residual level of 1%, it results in a 4×10^{-17} residual fractional EQ shift, which we also take as its uncertainty σ_{EQ}/f_0. The quadratic Zeeman shift correction uncertainty is $\sigma_{Z2}/f_0 = 1 \times 10^{-17}$. The scalar Stark shift's fractional value, 1×10^{-17}, may conservatively be taken as Stark uncertainty σ_S/f_0. The BBR shift is $\Delta f_{BB}/f_0 = -10 \times 10^{-17}$. The uncertainty σ_{BB,T_0} associated with the experimental uncertainty $\sigma_{T_0} = 8$ K of the BBR temperature is $\sigma_{BB,T_0}/f_0 = 4(\sigma_{T_0}/T_0)|\Delta f_{BB}|/f_0 \simeq 1 \times 10^{-17}$. In this example, the theoretical uncertainties of the shift coefficients are not significant. The dominant systematic uncertainty arises from the EQ shift.

In HD^+ we recently demonstrated that transitions with zero total angular momentum projection in the initial and final state, $J_z = 0 \rightarrow J'_z = 0$, are most favorable, since they exhibit a small quadratic Zeeman shift at low field [16] (and $\Delta\eta_B = 0$). We found no suitable transitions (within the reasonable requirement $v = 0, v' \leq 5$) having also particularly small electric quadrupole shift. This results (see the Supplemental Material, Sec. B [39]) in total uncertainties equal or larger than $\sigma_{\mathrm{syst},f_0}/f_0 = 3 \times 10^{-16}$, significantly larger than for $H_2{}^+$.

Before entering the discussion of the composite frequency method, we point out that the combination of just two suitably chosen transitions can already improve the accuracy. In the case of $H_2{}^+$, consider as an example the transition between the homologous states $(I = I' = 1, S = S' = 1/2, J = J' = 3/2, J_z = J'_z = \pm 1/2)$ and the transition between the homologous states $(I = I' = 1, S = S' = 3/2, J = J' = 5/2, J_z = J'_z = \pm 5/2)$ of $(v = 0, L = 1) \rightarrow (1, 1)$, having a transition frequency difference of 37.5 MHz. Their EQ shifts are almost equal and opposite, so that averaging over the two transitions reduces this shift to a negligible level even without use of the orthogonal field technique.

Details of the composite frequency method.—We now discuss in more detail the concept of composite frequency which allows reducing further the already small systematic shift uncertainties. In general, a composite frequency $f_c = \sum_i^N \beta_i f_i$ is free of Zeeman, quadrupole and Stark shift if the conditions, $\sum_i \beta_i \Delta\eta_{B,i} = 0$ (linear Zeeman effect for particular transitions of $H_2{}^+$) and/or $\sum_i \beta_i \Delta\eta_{B^2,i} = 0$ (quadratic Zeeman effect for particular transitions of HD^+ and $H_2{}^+$), $\sum_i \beta_i \Delta\eta_{Vzz,i} = 0$, $\sum_i \beta_i \Delta\alpha_i^{(l)} = 0$, $\sum_i \beta_i \Delta\alpha_i^{(t)} = 0$ are satisfied, respectively, assuming that the contributing individual transitions are selected as described above. For the homonuclear molecular hydrogen ions, the latter two conditions also eliminate the "composite" scalar polarizability and thus eliminate the (static) BBR shift, independently of the temperature T_0, since all individual shifts are proportional to T_0^4 in the static approximation. For HD^+ there is no such simple dependence [36], and the BBR shift cancellation constraint, for a particular temperature T_0, is $\sum_i \beta_i \Delta f_{BB,i}(T_0) = 0$, and represents an additional condition.

If we choose $N = M + 1 = 5$ transitions for ${\mathrm{H}_2}^+$ or $N = M + 1 = 6$ for HD^+ we find corresponding solutions $\{\beta_i\}$ (up to a common factor). But since there exists a large number ($\gg N$) of transitions with weak systematic shifts that may be employed, a large number K of solutions $\{\beta_i\}_K$ exists, with a corresponding transition set $\{i_1, \ldots, i_N\}_K$ for each. We may therefore further down-select the solutions according to additional criteria. Obviously, the accuracy of cancellation of the shifts depends on the inaccuracies of the theoretical shift coefficients $\sigma_{y,\Delta\eta_j}$ (which as shown above are small and will be reduced further with future theory work) and on the amount of variation σ_{y,X_j} of the perturbations in-between measurements of individual frequencies (which is to be minimized experimentally). We can then compute, for each solution, the total absolute uncertainty $\sigma_{\mathrm{syst},f_c} = \sum_j^M \sigma_j^2$ of the composite frequency,

$$\sigma_{\mathrm{syst},f_c}^2 = \sum_i^N \sum_j^M (\sigma_{y,\Delta\eta_{j,i}}^2 + \sigma_{y,X_j}^2 {n_j}^2) \beta_i^2 (\Delta\eta_{j,i} X_j^{n_j})^2, \quad (2)$$

[with the appropriate replacement for the contribution from the BBR shift of HD^+, $\beta_i^2 \{\sigma_{abs,\Delta f_{BB,i}}^2 + (\sigma_{y,T} T_0)^2 [d\Delta f_{BB,i}(T_0)/dT]^2\}$] and select a solution with a low value. We emphasize that for given shift coefficient uncertainties $\{\sigma_{y,\Delta\eta_{j,i}}\}$ and given experimental instabilities $\{\sigma_{y,X_j}\}$, a desired level of $\sigma_{\mathrm{syst},f_c}$ leads to conditions for the maximum permitted field strengths $\{X_j\}$.

Numerical results.—We have performed a numerical search for the composite frequency with lowest fractional systematic uncertainty $\sigma_{\mathrm{syst},f_c}/f_c$. We find that there are many solutions with very close values. Tables II and III in the Supplemental Material [39] give one example for each ion, which we now discuss. For ${\mathrm{H}_2}^+$ we limit the transition set to fundamental vibrational transitions, for which the light shift can be reduced to a negligible level, and further only to initial states in $v = 0$, which appear to be more easily prepared. Because transitions belonging to this set have similar differential polarizabilities and therefore also BBR shifts, the nulling of the composite BBR shift and Stark shift leads to a composite frequency f_c significantly smaller than the individual transition frequencies $f_{0,i}$ and therefore to a relatively large fractional uncertainty [40]. Instead, we consider simplified composite frequencies in which only the EQ, the linear and the quadratic Zeeman shifts are canceled ($M = 3$). If the linear Zeeman shift is canceled by probing, for each transition, the Zeeman pair as described above, a total of $N = 6$ transitions must be measured. (Alternatively, it is also possible to do so using a minimum of $N = 4$ transitions.) The solution shown in the Supplemental Material [39] includes only two vibrational transitions, reducing the number of required lasers to only two. The dominant uncertainties arise from the noncancellable shifts: the Stark shift is $|\Delta f_{S,f_c}/f_c| \simeq 1.2 \times 10^{-17}$, which we also take as the corresponding uncertainty, and the uncertainty of the BBR shift is nearly the same. The latter may be reduced either by better knowledge of the trap temperature, or by use of a cryogenic ion trap. The total uncertainty $\sigma_{\mathrm{syst},f_c}/f_c \simeq 1.6 \times 10^{-17}$ is approximately a factor 3 lower than for the single-transition example given above. The additional experimental effort is only moderately higher, with the advantage that the orthogonal quantization axis technique is unnecessary. Note that a small magnetic field $B = 0.07$ G is chosen. This value is still compatible with resolving individual Zeeman components, provided appropriate ultranarrow-linewidth lasers are employed.

In the case of HD^+, we show in the Supplemental Material [39] a particular solution where not the BBR shift but its derivative with respect to temperature is canceled, via the constraint $\sum_i \beta_i d\Delta f_{BB,i}(T_0)/dT_0 = 0$. We set $B = 0.02$ G but can relax the requirement for magnetic field instability $\sigma_{y,B}$ compared to the ${\mathrm{H}_2}^+$ case. This results in a composite BBR shift $\Delta f_{BB,f_c} = 4 \times 10^{-17}$. Its uncertainty is dominated by the theoretical uncertainties of the individual BBR shifts, resulting in $\sigma_{BB,\Delta f_{BB},f_c}/f_c = 2 \times 10^{-18}$. (As described above, this contribution can be reduced with future theory work.) We find a total uncertainty $\sigma_{\mathrm{syst},f_c}/f_c = 5 \times 10^{-18}$, limited by the uncertainty of the EQ shift. Alternatively, we can choose to cancel the BBR shift instead of its derivative, but find that the best solutions yield a moderately larger total uncertainty.

Extension of the method.—With the proposed approach, additional systematic shifts can in principle be compensated, as long as they are transition-dependent. This includes the light shift caused by the UV laser that cools the atomic ion, or the Zeeman shift contributions of higher order in B, if relevant. In case of the light shift caused by the spectroscopy laser(s) we must take into account that different transitions may require different lasers, which provide different, independent intensities at the molecular ion. The composite frequency method can be applied within a subset of all transitions contributing to the composite frequency, where a subset includes the hyperfine components of a single rovibrational transition. Such a subset would be interrogated sequentially by the same laser beam, appropriately frequency-tuned. The intensity can then be kept constant across the subset of transitions by maintaining the beam power constant since the beam size will typically not change upon small frequency changes. If this is done, the light shift may then be compensated for the subset. This can be applied to more than one subset, if necessary.

Conclusion.—We computed the external-field shift coefficients of the one-electron molecular ions ${\mathrm{H}_2}^+$ and HD^+, and have identified vibrational transitions in ${\mathrm{H}_2}^+$ having extremely low systematic shifts ($< 5 \times 10^{-17}$). Moreover, we have proposed to measure composite transition frequencies, selected by theoretical calculation to be free of external-field shifts. This approach should enable a systematic uncertainty as low as several 10^{-18} for HD^+, and $< 2 \times 10^{-17}$ for ${H_2}^+$. The expense of the composite frequency method is the need of performing spectroscopy and frequency measurements of at least $M + 1$ transitions (M being the number of systematic effects to be canceled), in different wavelength ranges. However, this is technologically feasible, as has been already shown in the case of HD^+ [2,3]. Thus, our theoretical analysis provides a strong motivation and guide to future experiments employing molecules to probe fundamental physics issues.

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[40] If fundamental transitions starting from $v > 0$ are included, the cancellation of the Stark and BBR shifts can be implemented effectively, with $< 1 \times 10^{-17}$ total systematic uncertainty.