

Candidate molecules for next-generation searches of hadronic charge-parity violation

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We systematically study a set of strongly polar heteronuclear diatomic molecules composed of laser-coolable atoms for their suitability as sensitive probes of new charge-parity violation in the hadron sector of matter. Using relativistic general-excitation-rank configuration-interaction theory we single out the molecule francium-silver (FrAg) as the most promising system in this set and calculate its nuclear Schiff-moment interaction constant to $W_{SM}^{\text{FrAg}}(\text{Fr}) = 30168 \pm 2504$ a.u. for the target nucleus Fr. Our work includes the development of system-tailored atomic Gaussian basis sets for the target atom in each respective molecule.

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I. INTRODUCTION

Electric dipole moments (EDM) are low-energy probes [1] very effectively used in the search for new sources of charge-parity (\mathcal{CP}) violation beyond those already implemented into the standard model (SM) of elementary particles through the Cabibbo-Kobayashi-Maskawa (CKM) formalism [2,3]. Complex physical systems like atoms and molecules offer distinct advantages in this search since the new sources of \mathcal{CP} violation can be magnified by many orders of magnitude [4–6]. The disadvantage of using a complex system lies in the multitude of possible underlying \mathcal{CP} -violating mechanisms creating the EDM at the atomic scale [7], making multiple measurements on different systems necessary in order to disentangle the possible sources.

In judiciously chosen atoms and molecules, however, leptonic \mathcal{CP} violation can be strongly suppressed, making these systems sensitive to the hadronic and certain semihadronic sources only [8]. At the nuclear energy scale one of the leading manifestations of this type of symmetry breaking is the nuclear Schiff moment [9,10].

The nuclear Schiff moment S scales [10,11] roughly as

$$S \propto \frac{\beta_2 \beta_3 Z A^{2/3}}{\Delta E_{\pm}}, \quad (1)$$

where β_2 and β_3 are nuclear quadrupole and octupole deformation parameters, respectively, Z is the proton number, A is the nucleon number, and ΔE_{\pm} is the energy splitting between opposite-parity doublets of nuclear states. The atomic or molecular interaction W of the nuclear Schiff moment

scales as [11] (for $s_{1/2} - p_{1/2}$ mixing)

$$W \propto Z^2 \frac{4\sqrt{1 - Z^2\alpha^2}}{\Gamma(2\sqrt{1 - Z^2\alpha^2} + 1)^2} \left(\frac{2ZR_N}{a_B} \right)^{2\sqrt{1 - Z^2\alpha^2} - 2}, \quad (2)$$

where α is the fine-structure constant, R_N is the respective nuclear radius, and a_B is the bohr radius. Highest sensitivity to new \mathcal{CP} -violating hadron physics can thus be achieved by using an atomic nucleus with both large proton number and large octupole deformation. Indeed, regions with nuclear isotopes fulfilling these conditions have been identified [12].

Sensitivity can be further enhanced by several orders of magnitude using a diatomic molecule built from an atom with a target nucleus fulfilling the above conditions, another atom with large electron affinity, and assuring that both of these atoms are laser coolable to very low temperatures [13]. In Ref. [14] a strong case has been made to use the diatomic molecule radium-silver (RaAg), which is composed of laser-coolable atoms in the search for new \mathcal{CP} violation of leptonic or semileptonic origin. It is thus plausible in the search for new hadronic sources to use a similar diatomic molecule, but modified such that the leptonic or semileptonic sources are suppressed. This can be achieved when the respective science state of the molecule is predominantly represented by a closed-electron-shell configuration. In that case the nucleon-electron scalar-pseudoscalar and electron electric dipole moment interactions, for instance, will only appear in higher orders of perturbation theory [15].

In this paper we present a systematic study of the Schiff-moment interaction in six diatomic molecules composed of laser-coolable atoms combined such that they have a polar bond and an electronically closed-shell ground state near their equilibrium internuclear configuration. The highly polarizable target atoms are represented by rubidium (Rb), cesium (Cs), and Fr. As partners with high electron affinity we choose lithium (Li) and Ag. The former atom is mainly included for establishing trends. For one of these molecules, FrAg, a large set of data relevant to the assembly and trapping in

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an ultracold environment has been presented recently [16]. Here we present calculations of Schiff-moment interactions in alkali-alkali-metal molecules.

The paper is structured as follows. In the following Sec. II we briefly review the theory of how we obtain molecular wave functions and how the Schiff-moment interaction is calculated using these wave functions. Section III comprises the main body where we discuss basis-set optimization for the different molecules and present results for the molecular Schiff-moment interaction. In the final Sec. IV we draw conclusions from our findings, discuss the expected impact of the results, and mention ongoing and future work.

II. THEORY: MOLECULAR SCHIFF-MOMENT INTERACTION CONSTANT

The calculation of the Schiff-moment interaction constant in the present molecules follows the implementation in Ref. [17].

The molecular \mathcal{P} , \mathcal{T} -violating energy shift due to a finite nucleus with assumed nuclear Schiff moment S_z along the molecular axis is written as [18]

$$\Delta\varepsilon_{\text{SM}} = -S_z \frac{3}{B} \left\langle \sum_{j=1}^n \hat{z}_j \rho(\mathbf{r}_j) \right\rangle_{\psi}, \quad (3)$$

where $B = \int_0^\infty \rho(\mathbf{r}) r^4 dr$ and $\rho(\mathbf{r})$ is the nuclear charge density at electron position coordinate \mathbf{r} . For a Gaussian nuclear density with exponent ζ we established that $B = \frac{3}{8\pi\zeta}$ in Ref. [17].

The molecular wave function is obtained from the zeroth-order problem

$$\hat{H}|\psi\rangle = \varepsilon|\psi\rangle, \quad (4)$$

with

$$\begin{aligned} \hat{H} &:= \hat{H}^{\text{Dirac-Coulomb}} \\ &= \sum_j^n \left[c \boldsymbol{\alpha}_j \cdot \mathbf{p}_j + \beta_j c^2 - \sum_K^2 \frac{Z_K}{r_{jK}} 11_4 \right] \\ &\quad + \sum_{k>j}^n \frac{1}{r_{jk}} 11_4 + V_{KL} \end{aligned} \quad (5)$$

for a diatomic molecule with n electrons, where K runs over nuclei and V_{KL} is the classical electrostatic potential energy for the two Born-Oppenheimer-fixed nuclei. The CI expansion of the electronic wave function reads

$$\psi \hat{=} |\Omega\rangle = \sum_{I=1}^{\dim \mathcal{F}^I(M,n)} c_{(\Omega),I} (\overline{S\mathcal{T}})_{(\Omega),I} |I\rangle, \quad (6)$$

where $|I\rangle$ is the true vacuum state, $\mathcal{F}^I(M,n)$ is the symmetry-restricted sector of Fock space (M_I subspace) with n electrons in M four-spinors, $\mathcal{S} = a_1^\dagger a_j^\dagger a_k^\dagger \dots$ is a string of spinor creation operators, and $\overline{\mathcal{T}} = a_1^\dagger a_m^\dagger a_n^\dagger \dots$ is a string of creation operators of time-reversal transformed spinors. The determinant expansion coefficients $c_{(\Omega),I}$ are generally obtained as described in Refs. [19,20], where Ω is the total angular momentum projection onto the internuclear axis. The Schiff-moment interaction

constant for a target nucleus A of a molecule is then written as

$$W_{\text{SM}}(A) := \frac{\Delta\varepsilon_{\text{SM}}(A)}{S_z(A)} = -\frac{3}{B} \left\langle \sum_{j=1}^n \hat{z}_j \rho_A(\mathbf{r}_j) \right\rangle_{\psi}. \quad (7)$$

In practical applications A is placed at the origin of the reference frame.

The KRCI module of the DIRAC program package [21] is used for the evaluation of required property integrals [22,23].

III. SCHIFF-MOMENT INTERACTIONS IN ALKALI-LITHIUM AND ALKALI-SILVER MOLECULES

A. Technical details

All the numerical calculations presented here were made using a locally modified version of the DIRAC program package [21]. The correlated calculations were carried out through the configuration-interaction (CI) method with the KRCI module [22]. We also use a spin-orbital singles and doubles coupled cluster method with perturbational triples corrections [CCSD(T)] via the RELCCSD module [24] for the geometry optimization of some of the studied molecules.

For the target atoms Rb, Cs, and Fr we use Dyal's quadruple-zeta (QZ) sets with all correlating and dipole-polarizing functions for shells $3d$ through $5s$, $5p$ added to the primitive set for Rb, all valence- and available outer-core correlating functions from $n = 4$ onward added for Cs, and all dipole polarization functions and outer-core correlating functions from $n = 5$ onward added for Fr [25]. For Cs and Fr we also used the corresponding Dyal's double-zeta (DZ) and triple-zeta (TZ) sets for comparative purposes [25]. For Li the EMSL basis sets of cc-pVNZ-DK type with $N \in \{2, \dots, 4\}$ are employed [26]. The Ag atom is described by the same QZ basis set as used in Ref. [14].

To read this paper, one should know the system of notation we use for the different CI models. The general form here is $Si_SDj_SDTk_x$ a.u. This means that we have i electrons in shells from which single excitations are performed, j electrons in accumulated shells with single and double excitations, and k electrons in accumulated shells with single, double, and triple excitations. x stands for the energy at which we truncate the complementary space.

B. Geometry optimization

In order to have a more accurate interpretation of future experiments, \mathcal{P} , \mathcal{T} -odd interactions should be evaluated at the equilibrium internuclear distance R_e for each of the diatomic molecules. Vibrational fluctuations of these molecular constants are much smaller than other uncertainties in our calculations.

For the RbLi and FrLi molecules we find the energy-curve minimum by fitting a polynomial to respectively 9 (RbLi) and 7 (FrLi) calculated CCSD(T) data points in a range from 5.8 a.u. to 6.7 a.u. (RbLi) and 6.5 a.u. to 7.1 a.u. (FrLi), respectively. The results obtained are shown in Table I, along with literature values for the other four molecules. For RbLi our result agrees with literature results [27–29] to within 1.5%. For FrLi a very recent Fock-space CC calculation [30] using

TABLE I. R_e from CCSD(T) calculation; (*) value taken from RCCSD(T) calculations in Ref. [31]; (†) Dirac-Coulomb CCSD(T) with 22 active electrons [32].

Molecule	RbLi	CsLi	FrLi	RbAg	CsAg	FrAg
R_e (a.u.)	6.527	6.927 [†]	6.878	5.845*	6.112*	6.190*

relativistic pseudopotentials deviates from our result by less than 1%.

C. Basis-set optimization

In this section we will demonstrate the necessity to do a basis-set optimization and discuss how it is carried out.

1. Deficiency of standard basis sets

The results in Table II demonstrate that small atomic basis sets (cvDZ) yield spurious results for W_{SM} , confirming earlier findings [17]. Even though the cvQZ basis produce a result physically acceptable for CsLi and FrAg molecules, it is not converged yet. Furthermore, the cvQZ basis produces a physically unacceptable result for the RbLi molecule. Therefore, even a cvQZ basis can fail to describe the physics of the Schiff-moment interaction in a qualitatively correct manner. We thus optimized target-atom basis sets in the molecular framework for each of the considered molecules.

2. Basis-set optimization itself

We follow the procedure proposed in Ref. [17]. This densification procedure allows us to generate a basis set that resembles quintuple-zeta (5Z) quality in the absence of a fully optimized 5Z basis set for the target atom. However, we have to determine individually when to truncate the densification procedure. This is done at the DCHF level considering both convergence of W_{SM} as well as stability of total energy.

For the RbLi and RbAg molecules (Tables III and IV), we can see a 4% change when going from 3sp to 4sp and, respectively, 0.3% and 0.1% when going from 4sp to 5sp. Meanwhile, the energy is converged at 10^{-6} a.u. Thus we chose a d-cvQZ+4sp augmented Dyal QZ basis that we denote cvQZ+ for the following when concerning those molecules.

For the CsLi and CsAg molecules (Tables III and IV), W_{SM} changes when going from 1sp to 2sp level by less than 0.1%, while the energy is converged at 10^{-6} a.u. In the following, cvQZ+ will be a short version of d-cvQZ+1sp when referring to those molecules.

For the FrLi and FrAg molecules (Tables III and IV) we observe one order of magnitude difference for W_{SM} between 0sp and other densification levels because the basis is not complete enough to describe the physics of the interaction. However, the W_{SM} change when going from 1sp to 2sp is, respectively, about 0.2% and 0.7%. In addition, according to the convergence at 10^{-5} a.u. of the energy, the d-cvQZ+1sp basis is an optimal singly-densified basis and the one we will use and denote as cvQZ+ for those molecules.

D. Correlated calculations

Now that we have all the optimized basis sets for our six molecules, we present and discuss results including interelectron correlation effects obtained using the CI method with various models.

1. Alkali-metal atoms bound to Li

In Tables V, VI, and VII are shown the results from our calculations on the different alkali-metal-Li diatomic molecules. These include various CI models and show the corresponding value for W_{SM} .

First of all, general trends for electron correlation effects established in Ref. [17] are also observable in the present systems: including excitations out of shells that directly contribute to $s-p$ mixing diminishes the interaction constant and this comprises the principal correlation effect in all studied molecules. Furthermore, from these tables we can directly see that the heavier the target atom, the higher the molecular Schiff-moment interaction constant. Indeed, with equivalent models for the three molecules we obtained W_{SM}^{RbLi} (Rb, SD22_9.9 a.u.) = 814 a.u., W_{SM}^{CsLi} (Cs, SD22_10 a.u.) = 2813 a.u., and W_{SM}^{FrLi} (Fr, SD22_10 a.u.) = 24414 a.u. The models are equivalent because they correlate the valence shell and the $(n-1)s$, $(n-1)p$, and $(n-2)d$ target atom shells and the 2s Li shell. There is roughly a factor of 3.5 difference between RbLi and CsLi and a factor of 30 difference between RbLi and FrLi. Such a trend was expected and confirms the scaling of the Schiff-moment interaction given in Eq. (2).

Francium is thus a very good choice of target atom for a Schiff-moment sensitive molecule since the resulting molecular constant is 8.3 times larger than with cesium.

2. Alkali-metal atoms bound to Ag

In Tables VIII, IX, and X are shown the results from our calculations on the different alkali-metal-Ag diatomic molecules. These include various CI models and their corresponding values for W_{SM} .

TABLE II. W_{SM} with double-, triple-, and quadruple-zeta basis set at the DCHF level for RbLi, CsLi, and FrAg.

Basis	RbLi ($R_e = 6.527$ a.u.)		CsLi ($R_e = 6.927$ a.u.)		FrAg ($R_e = 6.190$ a.u.)	
	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)
cvDZ	-2987.2228737	-1829.3	-7794.1925854	-10110.1	-29622.7980959	5946
cvTZ	-2987.2366325	-2144.5	-7794.2033064	-2848.8	-29622.8345496	28173
cvQZ	-2987.2370600	-1150.7	-7794.2038442	2098.1	-29622.8362766	29451

TABLE III. Singly-densified-cvQZ basis-set determination: DCHF for $^1\Sigma_0$ for three alkali-metal-Li molecules.

Basis	RbLi ($R_e = 6.527$ a.u.)		CsLi ($R_e = 6.927$ a.u.)		FrLi ($R_e = 6.878$ a.u.)	
	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)
cvQZ	-2987.2370600	-1150.7	-7794.2038442	2098	-24315.6247270	24004
d-cvQZ+0sp	-2987.2370672	-1183.4	-7794.2038120	1761	-24315.6219173	242340
d-cvQZ+1sp	-2987.2370734	-414.6	-7794.2038394	2887	-24315.6237748	25434
d-cvQZ+2sp	-2987.2370747	389.9	-7794.2038393	2885	-24315.6237716	25393
d-cvQZ+3sp	-2987.2370749	808.1	-7794.2038393	2891	-24315.6237716	25328
d-cvQZ+4sp	-2987.2370752	844.5	-7794.2038393	2883	-24315.6237714	25233
d-cvQZ+5sp	-2987.2370751	842.0	-7794.2038393	2894	-24315.6237716	25341
d-cvQZ+6sp	-2987.2370750	842.8	-7794.2038393	2884		
d-cvQZ+7sp	-2987.2370750	842.3	-7794.2038393	2887		
d-cvQZ+8sp	-2987.2370750	843.0	-7794.2038393	2888		

First of all, we can compare the alkali-metal-Ag diatomic molecule with the corresponding alkali-metal-Li diatomic molecule. At the valence-shell level, the $W_{\text{SM}}^{\text{alkali-metal-Ag}}$ (alkali-metal) value is roughly 1.25 times larger than the corresponding $W_{\text{SM}}^{\text{alkali-metal-Li}}$ (alkali-metal) one. This can largely be explained by the difference in electron affinity (EA) between Ag and Li [33,34]. Indeed, since the EA of the silver atom is twice as big as the lithium EA, the partial negative charge forming on the polarizing atom partner is significantly greater when Ag is used instead of Li. This axial distortion of the electron cloud is accompanied by mixing of predominantly s and p spinors and consequently leads to differences in the Schiff moment interaction. In particular, in the FrAg molecule, we find an atomic weight of p_z character of 10.8% on the total atomic Fr sp_z character, whereas in the FrLi molecule the p_z weight is only 5.8%. This quantitative comparison corroborates the above qualitative interpretation.

So far we have shown that the francium atom is a good target atom and that the silver atom is a good perturber atom. Thus we mainly focus on the FrAg molecule in the following analysis and interpretation.

In addition to Schiff-moment interaction constants we display total CI energies in Table X to show the magnitude of correlation energies in the various shells and to verify that our calculations are in accord with the variation theorem of quantum mechanics. Our results for $W_{\text{SM}}^{\text{FrAg}}(\text{Fr})$ show the

expected pattern for electron correlation effects. Replacements out of the outermost shells that contribute directly to $s - p$ mixing reduce the Schiff-moment interaction (CI models SD2 and SD10). This principal effect amounts to about -4.5% . In line with this interpretation, double excitations from the $4d$ Ag shell (model SD12) lead to an increase by about 1% relative to the model SD2. If correlations between the $4d$ Ag and the $6s6p$ Fr electrons are taken into account (model SD20) this increase is roughly halved.

Adding the $5d$ Fr and $4p$ Ag shells to all of the above comprises the model SD36, which increases $W_{\text{SM}}^{\text{FrAg}}(\text{Fr})$ by about 0.4% relative to the model SD20 and gives the value of 30239 a.u. at an 8 a.u. cutoff in the complementary space. In view of these results the following core shells are expected to give only minor corrections due to large energy denominators. In addition to this, compensations between effects that increase and those that quench $W_{\text{SM}}^{\text{FrAg}}(\text{Fr})$ will further diminish the additional corrections not taken into account in our explicit models.

Concerning the truncation of virtual spinors with the model SD36 we observe a difference between cutoff at 5 a.u. and cutoff at 8 a.u. of only 0.3% in $W_{\text{SM}}^{\text{FrAg}}(\text{Fr})$. Since the effect due to this change in cutoff is of the same magnitude as the change between the two most encompassing correlation models, SD20 and SD36, we consider it unnecessary to include virtual spinors of higher energy in the wave-function expansion.

TABLE IV. Singly-densified-cvQZ basis-set determination: DCHF for $^1\Sigma_0$ for three alkali-metal-Ag molecules.

Basis	RbAg ($R_e = 5.845$ a.u.)		CsAg ($R_e = 6.112$ a.u.)		FrAg ($R_e = 6.190$ a.u.)	
	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)	ϵ_{DCHF} (a.u.)	W_{SM} (a.u.)
cvQZ	-8294.4487693	-1445.2	-13101.4159681	2594.2	-29622.8363749	29475
d-cvQZ+0sp	-8294.4487772	-1313.8	-13101.4159361	2742.2	-29622.8335672	193210
d-cvQZ+1sp	-8294.4487834	-493.3	-13101.4159635	3593.8	-29622.8354237	31349
d-cvQZ+2sp	-8294.4487846	486.5	-13101.4159634	3589.2	-29622.8354202	31143
d-cvQZ+3sp	-8294.4487848	1015.6	-13101.4159635	3580.5	-29622.8354203	31085
d-cvQZ+4sp	-8294.4487850	1058.7	-13101.4159634	3576.2	-29622.8354201	31039
d-cvQZ+5sp	-8294.4487849	1057.2	-13101.4159634	3585.1	-29622.8354203	31094
d-cvQZ+6sp	-8294.4487849	1059.2				
d-cvQZ+7sp	-8294.4487849	1057.5				
d-cvQZ+8sp	-8294.4487849	1059.0				

TABLE V. RbLi, $^1\Sigma_0$, $R_e = 6.527$ a.u.

Basis/cutoff	W_{SM} (a.u.)
cvQZ+/DCHF	844.5
cvQZ+/SD2_9.9 a.u.	819.1
cvQZ+/SD10_9.9 a.u.	823.8
cvQZ+/SD22_9.9 a.u.	814.0

As we have demonstrated at the CISD level around 80% of total correlation effects are contributed by the valence and $6s6p$ Fr shells. Thus it is of interest to look at a higher-level model to the correlations arising from these electrons. The model SDT10 adds the full set of triple excitations to the model SD10 and increases the drop in $W_{SM}^{FrAg}(Fr)$ from the SD10 model by about 7%, indicating that even higher excitations should be rather unimportant.

In order to obtain a final value for $W_{SM}^{FrAg}(Fr)$ we use the model SD36 as a basis to which we add a triples correction:

$$W_{SM}^{FrAg}(Fr, SD36_8 \text{ a.u.}) - W_{SM}^{FrAg}(Fr, SD10_8 \text{ a.u.}) + W_{SM}^{FrAg}(Fr, SDT10_8 \text{ a.u.}) = 30168 \text{ a.u.} \quad (8)$$

To this final value we attribute an uncertainty of 8.3% coming from the different physical approximations and models used. 6.4 parts in these 8.3% are attributed to basis-set incompleteness, 0.9 parts to the correlation models used (cutoff, number of electrons correlated, and excitation rank) and 1 part is attributed to the physical approximation in the Hamiltonian. Each individual contribution to the uncertainty comes from the difference between the best and the second best models for a given effect. The part attributed to the physical approximation in the Hamiltonian is due to the lacking Breit term and other higher-order terms, usually considered to be of the percent approximation [35]. Thus the final value we obtain including its uncertainty is $W_{SM}^{FrAg}(Fr) = 30168 \pm 2504$ a.u., assuming that further uncertainty associated with the operator [18] describing the interaction of the Schiff moment with the electron shells is negligible.

IV. CONCLUSIONS AND OUTLOOK

We summarize results for Schiff moment interaction constants in the six molecules under investigation in Table XI. For FrAg the final result is given and for the other molecules the results from the respective model using the largest number of correlated electrons.

We establish the FrAg diatomic molecule as an excellent probe in the search for new sources of hadronic \mathcal{CP} violation. The use of an Ag atom as polarizing partner increases

TABLE VI. CsLi, $^1\Sigma_0$, $R_e = 6.927$ a.u.

Basis/cutoff	W_{SM} (a.u.)
cvQZ+/DCHF	2886.9
cvQZ+/SD10_10 a.u.	2795.1
cvQZ+/SD8_SDT10_10 a.u.	2844.2
cvQZ+/SD22_10 a.u.	2813.4

TABLE VII. FrLi, $^1\Sigma_0$, $R_e = 6.878$ a.u.

Basis/cutoff	W_{SM} (a.u.)
cvQZ+/DCHF	25434
cvQZ+/SD2_2 a.u.	24288
cvQZ+/SD2_5 a.u.	24282
cvQZ+/SD2_10 a.u.	24287
cvQZ+/SD10_10 a.u.	24245
cvQZ+/S10_SD22_10 a.u.	24289
cvQZ+/SD22_10 a.u.	24414

TABLE VIII. RbAg, $^1\Sigma_0$, $R_e = 5.845$ a.u.

Basis/cutoff	W_{SM} (a.u.)
cvQZ+/DCHF	1059.1
cvQZ+/SD2_2 a.u.	1036.8
cvQZ+/SD2_6.8 a.u.	1036.7
cvQZ+/SD2_11 a.u.	1036.8
cvQZ+/S10_SD12_11 a.u.	1015.0
cvQZ+/SD12_11 a.u.	1041.9

TABLE IX. CsAg, $^1\Sigma_0$, $R_e = 6.112$ a.u.

Basis/cutoff	W_{SM} (a.u.)
cvQZ+/DCHF	3593.4
cvQZ+/SD2_2 a.u.	3503.8
cvQZ+/SD2_11 a.u.	3502.3
cvQZ+/S10_SD12_2 a.u.	3446.6
cvQZ+/S10_SD12_5.5 a.u.	3423.5
cvQZ+/S10_SD12_11 a.u.	3420.9
cvQZ+/SD12_11 a.u.	3529.6

TABLE X. FrAg, $^1\Sigma_0$, $R_e = 6.190$ a.u.

Basis/cutoff	ϵ_{CI} (a.u.)	W_{SM} (a.u.)
cvQZ+/DCHF	-29622.8354238	31350
cvQZ+/SD2_2 a.u.	-29622.8604657	30359
cvQZ+/SD2_3 a.u.	-29622.8605116	30349
cvQZ+/SD2_5 a.u.	-29622.8605445	30355
cvQZ+/SD2_8 a.u.	-29622.8605500	30360
cvQZ+/SD10_8 a.u.	-29623.0196812	29980
cvQZ+/SDT10_8 a.u.	-29623.0260848	29909
cvQZ+/SD12_8 a.u.	-29623.1920759	30711
cvQZ+/SD20_8 a.u.	-29623.3371101	30127
cvQZ+/SD36_5 a.u.	-29623.7102434	30333
cvQZ+/SD36_8 a.u.	-29623.8379481	30239

TABLE XI. Summary table for the six studied molecules. The "final" model for the FrAg molecule is the same as in Eq. (8).

System	Model	W_{SM} (a.u.)
FrAg	Final	30168
CsAg	cvQZ+/SD12_11 a.u.	3529.6
RbAg	cvQZ+/SD12_11 a.u.	1041.9
FrLi	cvQZ+/SD22_10 a.u.	24414
CsLi	cvQZ+/SD22_10 a.u.	2813.4
RbLi	cvQZ+/SD22_9.9 a.u.	814.0

the molecular Schiff-moment interaction by nearly 25% as compared to the more standard [36] and also significantly electron-affine Li atom as polarizing partner in the FrLi molecule.

FrAg consists of laser-coolable atoms that form a strongly polar molecular bond and exhibit a molecular Schiff-moment interaction that is only roughly 25% weaker than the same interaction in the thallium monofluoride (TlF) molecule [37], the molecule currently in use in a leading hadron-sector \mathcal{CP} -violation search. According to our DCHF calculations of the respective ground states of TlF and FrAg the partial negative charge on F in TlF is significantly greater than on Ag in FrAg. Alongside this greater polarization the amount of $s - p$ mixing in TlF is also greater than in FrAg in the outermost valence spinors, largely explaining the difference in the Schiff-moment interaction constant. Nevertheless, using a molecule assembled from laser-coolable atoms [14] instead of a molecular beam and a target nucleus with strong octupole deformation should greatly outweigh this rather modest disadvantage. The advantage is due to long spin-coherence times for relatively large molecular ensembles provided by

optical trapping of (ultra)cold atoms [38]. Furthermore, ^{205}Tl is not located in the region of strongly octupole-deformed nuclei [12]. It has been shown [39,40] that the dependency of the Schiff moment of ^{205}Tl on underlying CPV parameters such as QCD Θ and the π -meson exchange constants is some orders of magnitude smaller than the same dependency of the Schiff moment of $^{223}\text{Fr}^+$. Taken together, several orders of magnitude in sensitivity can be gained by using FrAg instead of TlF in a molecular experiment.

In ongoing work we are exploring systematically the effect of replacing the Gaussian nuclear density used for Schiff-moment interactions thus far by a more accurate Fermi distribution. Moreover, we are studying an important semihadronic EDM source—the nucleon-electron tensor-pseudotensor (Ne-TPT) interaction in scientifically relevant molecules using the atomic basis sets optimized in the present work.

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