INTRODUCTION

The principle advantage of using heavy-atom, polar, diatomic molecules for searching for space parity violation interactions ($P$-odd interactions) and simultaneously space parity and time reversal violating forces ($P, T$-odd forces) is known for more than 30 years. Nevertheless, only the latest generation of molecular experiments finally surpassed their atomic competitors in sensitivity to one of the most important $P, T$-odd properties of elementary particles, namely the permanent electric dipole moment of an electron (eEDM) [1] (see also the recent report on preliminary data for ThO which claims an improved restriction on the eEDM by almost an order of magnitude [2]). Whereas molecules are ideally tailored to create favourable, well-defined fields at the heavy nucleus, the complexity of measurements with molecules is typically connected with various systematic effects which can mimic $P$-odd correlations. This calls for an active identification of promising molecular candidates that allow different approaches to suppress systematic effects. In the search for an eEDM, experimentally oriented re-search groups are currently focussing on YbF [1], PbO $^2$, ThO $^2$, WC $^3$, PbF $^6$ molecules and HfH$^+$ molecular ion $^5$. In all these experiments, high-quality electronic structure calculations are crucial both for the preparation stage of the experiment and for subsequent interpretation of experimental data obtained $^5$.

Another set of pivotal molecular experiments is connected with attempts to measure the nuclear anapole moment, a $P$-odd electromagnetic form-factor appearing in $I > 0$ nuclei due to $P$-odd nuclear forces. The only nucleus, for which the anapole moment was successfully determined, is $^{133}$Cs. In this experiment a vapour of Cs atoms was employed $^2$. The results are apparently in disagreement with the earlier measurement on Tl atom $^{10, 11}$. Currently molecular experiments are under development in Yale on BaF $^5$ and in Groningen on SrF $^{12}$.

DIRECT COOLING OF MOLECULES WITH LASERS

We identified earlier a set of requirements on molecular electronic structure for molecules being suitable for direct cooling with lasers $^{13}$. Monofluorides of group II elements (e.g. BaF and RaF) belong to the first class of molecules with highly diagonal Frank-Condon matrix. One problem emerging, however, in lasercooling of BaF molecule (isovalent to RaF) is connected with the existence of a metastable $^2\Delta$ level, lying energetically below the $^2\Pi$ level involved in the optical cooling loop. Our previous electron correlation calculations of the spectroscopic parameters in RaF indicated that the energetically lowest electronically excited level is $^2\Delta$. We took now larger atomic basis sets and active spaces of virtual molecular orbitals to investigate the stability of the ordering of electronic levels. The results are summarized in Table I. These show that even considerable alterations in the parameters of the Fock-space relativistic coupled cluster (FS-RCC as implemented in DIRAC program package $^{14}$) calculations do not change the ordering of levels in RaF. On the other hand FS-RCC, calculations of BaF with a basis set of similar quality as for RaF and as large active spaces (see supplementary material) confirm the first excited electronic level in BaF to be $^2\Delta$. Based

Recently, we identified the open-shell diatomic molecule RaF as an exceptionally suitable candidate for nuclear anapole moment measurements, having on the one hand a high enhancement factor for nuclear spin-dependent weak interaction and on the other hand offering potential for direct cooling with lasers. In the present work we demonstrate that RaF presents unique possibilities for measurements of $P$-odd and $P, T$-odd effects due to favourable combinations of peculiarities of molecular electronic structure and nuclear structure of radium isotopes.

Lasercooled radium monofluoride: A molecular all-in-one probe for new physics

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The particular advantages of using the diatomic molecular radium monofluoride (RaF) as a versatile molecular probe for physics beyond the Standard Model are highlighted. i) RaF was previously suggested as being potentially amenable to direct cooling with lasers. As shown in the present work, RaF’s energetically lowest electronically excited state is of $^2\Pi$ symmetry (in contrast to BaF), such that no low-lying $^2\Delta$ state prevents efficient optical cooling cycles. ii) The effective electric field acting on the unpaired electron in the electronic ground state of RaF is estimated larger than in YbF, from which the best restrictions on the electron electric dipole moment (eEDM) were obtained experimentally. iii) Favourable crossings of spin-rotational levels of opposite parity in external magnetic fields exist, which are important for the measurement of the nuclear anapole moment of nuclei with a valence neutron. Thus, RaF appears currently as one of the most attractive candidates for investigation of parity-odd as well as simultaneously parity- and time-reversal-odd interactions in the realms of molecular physics.
and 26 a different 4-component all-electron uncontracted basis set on ANO basis set by Roos et al. The active space in FS-CCSD material for computational details and references). And for RCC-ANO up to 1000 Hartree (see supplementary material for computational details and references). On comparison to experimental BaF results we estimate the accuracy of $T_0$ calculation for RaF to be within 1200 cm$^{-1}$ (without changing the ordering of the levels), $R_e$ within about 0.1 $a_0$ and $\omega_e$ about 60 cm$^{-1}$.

### TABLE I. Estimated molecular spectroscopic parameters for the electronic ground state $^2\Sigma_{1/2}$ and the first electronically excited state from FS-CCSD calculations of $^{226}$RaF and $^{137}$BaF. 17 electrons are correlated in both cases: $2p_{1/2,3/2}$ and $2s_{1/2}$ on fluorine, $5s_{1/2}$, $5p_{1/2,3/2}$ and $6s_{1/2}$ and Ba and $6s_{1/2}$, $6p_{1/2,3/2}$ and $7s_{1/2}$ an Ra. The results are given for two different 4-component all-electron uncontracted basis sets on Ra and Ba atom: Dyall’s relativistic basis set and the RCC-ANO basis set by Roos et al. The active space in FS-CCSD was restricted by energy for Dyall’s basis set up to 10 Hartree and for RCC-ANO up to 1000 Hartree (see supplementary material for computational details and references).

| Basis Set          | $^2\Sigma_{1/2}$ | $^2\Pi_{1/2}$ | $^2\Pi_{3/2}$ | $^2\Delta_{3/2}$ | $^2\Delta_{5/2}$ |
|--------------------|------------------|---------------|---------------|------------------|------------------|
| RaF: Dyall         | 4.24$^a$         | 4.24$^a$      | 4.24$^a$      | 4.25             | 4.27             |
|                   | 428$^a$          | 432$^a$       | 410           | 432              | 419              |
|                   | 1.40$^a$         | 1.60          | 1.64          | 1.71             | 1.81             |
| RaF: RCC-ANO       | 4.29             | 429           | 4.31          | 4.28             | 4.30             |
|                   | 431              | 428           | 415           | 431              | 423              |
|                   | 1.33             | 1.50          | 1.54          | 1.58             | 1.67             |
| BaF: RCC-ANO       | 4.15             | 421           | 4.21          | 4.21             | 4.23             |
|                   | 456              | 455           | 455           | 444              | 455              |
|                   | 1.09             | 1.13          | 1.17          | 1.24             | 1.42             |
|                   | (from Ref. [15] if not indicated otherwise) | | | | |
| $^2\Sigma_{1/2}$  | 4.09$^d$         | 469$^d$       | 4.68 ± 0.07$^d$ |
| $^2\Delta$        | 437              | 1.09        |
| $^2\Pi$           | 4.13$^e$         | 437          | 1.17          |
| $^2\Sigma$        | 4.17$^e$         | 424          | 1.3828        |

a) Ref. [13]; b) Ref. [16]; c) Supplementary material of Ref. [16]; d) Ref. [17]; e) Ref. [18]

### LEVEL CROSSING IN MAGNETIC FIELD AND SENSITIVITY TO THE NUCLEAR ANAPOLE MOMENT

$\mathcal{P}$-odd effects in diatomic molecules can be greatly enhanced by shifting levels of opposite parity to near-crossing with the help of external magnetic fields [19]. This idea is exploited in [3] for measurement attempts of the nuclear anapole moment in BaF. One of the main problems in the suggested approach is to create highly homogeneous magnetic fields in large volumes. Favorable values of magnetic fields required to tune spin-rotational levels to near crossing would be below 10 kG (1 T), as creation of larger magnetic flux densities require special effort, for instance superconducting magnets. To estimate if fields with $|B| < 1$T suffice to create near level crossings in RaF we calculated Zeeman splittings for spin-rotational levels (See Fig. 2 and Fig. 3 in supplementary materials). Matrix elements of the spin-rotational Hamiltonian in magnetic field were implemented as in Ref. [20]. The following parameters of the spin-rotational Hamiltonian were employed: rotational constant $B_e = 5689$ MHz (as calculated from equilibrium structure), ratio of spin-doubling constant $\Delta \approx 2B$, $\Delta / 2B = 0.97$ (as calculated within a four-component Dirac–Hartree–Fock approach), components of the hyperfine tensor for $^{225}$Ra nucleus $A_\parallel = -15100$ MHz and $A_\perp = -14800$ MHz (calculated with the two-component zeroth order regular approximation (ZORA) approach as implemented in a modified version of the program package TURBOMOLE [21]; values were already used for scaling in Ref. [16], but not explicitly reported therein) and components of $G$-tensor $G_\parallel = 1.993$ and $G_\perp = 1.961$ (crude estimate based on results for HgH). According to our calculation, the first crossing of levels of opposite parity takes place at about 3 kG for levels with the projection $F_z$ of the total angular momentum on the direction of the magnetic field being $-3/2$. A few more crossings take place in fields up to 10 kG for levels with $F_z = -1/2$, thus providing additional freedom for choosing the optimal experimental parameters.

To estimate the lowest possible flux of RaF molecules, which allows to measure the anapole moment in RaF, one needs to find the ratio $\Delta W / W$ with $W$ being the experimentally measured signal proportional to the matrix element of the nuclear spin-dependent weak interaction $W_\alpha$, and $\Delta W$ its experimental uncertainty. The condition for meaningful measurement is $\Delta W / W < 1$. We assume that the experimental scheme employed for measurement of the anapole moment is analogous to the one suggested in [3]. According to [3] the maximal value of $\Delta W / W$ is

$$\frac{\Delta W}{W} \approx \frac{1}{2\sqrt{2N_0}2F\tau},$$

with $N_0$ being the total number of molecules ($N_0 = F\tau$, where $F$ is the detected molecular flux and $\tau$ is the to-
tal measurement time) and $t$ the interaction time between molecule and external fields. Thus one gets $F > 1/(8 W^2 t^2 \tau)$. The time for molecular trapping can reach a few seconds [22], so let $t = 1\, s$, $\tau = 1\, h = 3600\, s$. To estimate $W$ we just scale the value for Ba given in Ref. [3], as $W_{Ba}/W_{Ra} \simeq W_{Ba}/W_{Ra}^2$, and take $W_{Ra} \simeq 10 W_{Ba} = 50\, Hz$. The least required flux of RaF is roughly then $F = 1/(8 \cdot 2500 \cdot 1 \cdot 3600)\, s^{-1} = 1.4 \cdot 10^{-8}\, s^{-1}$. In practice one might expect trapping and detection of at least one molecule during an experiment time of $\tau = 1\, h$ (see below), corresponding to a flux of $2.8 \cdot 10^{-4}\, s^{-1}$, which is a few orders of magnitude higher than the least required flux of RaF. This implies that it should be possible to perform successful measurements with signals from single trapped RaF molecules.

**EFFECTIVE ELECTRIC FIELD ACTING ON THE UNPAIRED ELECTRON IN RAF**

One of the most important parameters in molecular experiments on eEDM is the effective electric field $E_{\text{eff}}$ acting on the unpaired electron in the electronic ground state of the molecule of interest. This field, however, can not be measured directly in experiment, but is predicted from quantum chemical calculations. We estimate here the effective electric field acting on the unpaired electron in RaF by using relations between matrix elements of different $P$-odd and $P, T$-odd operators as it has been done in Ref. [23] by Kozlov and extended recently in Ref. [24]. According to the semiempirical model of Kozlov [23] the relation between the parameter $W_s$ of the $P, T$-odd term and the parameter $W_a$ of the $P$-odd term in the effective spin-rotational Hamiltonian is

$$W_s/W_a = Z \gamma/(2\gamma + 1),$$

where $Z$ is the nuclear charge number and $\gamma = \sqrt{1 - (\alpha Z)^2}$. As one can see from the Table II this relation provides good agreement with the results of explicit calculations of the $W_s$ by a two-component ZORA generalized Hartree–Fock (GHF) method for BaF, YbF and RaF molecules. On the other hand for HgH and CnH there exists a bigger discrepancy between estimated and calculated $W_s$. This can be attributed to the influence of the core-valence polarisation, which also contributes considerably to the $W_a$ values as noted in [16]. To clarify the situation with the scalar $P, T$-odd interaction in HgH and CnH one needs high-precision correlation calculations, similar to those in [25].

Matrix elements $M_{SPT}$ of the scalar $P, T$-odd interaction and matrix elements $M_{EDM}$ of the coupling between eEDM and inner molecular electric field are given in [24].

Relations between these M.E.’s can be also expressed through relativistic enhancement factor $R(Z)$ [26], which reflects the impact of relativistic effects on molecular electronic structure (see e.g. [10] on the influence of $R(Z)$ on $W_a$ for a range of diatomic molecules). The relation reads as

$$C_{SP} \frac{M_{EDM}}{(d_e/(ea_0)) M_{SPT}} = \frac{(1 - 0.283 a^2 Z^2)^2}{(1 - 0.56 a^2 Z^2)^2} \frac{16 \sqrt{2\pi} Z \alpha}{3 A(G_F/(E_h a_0^3))} \frac{2\gamma + 1}{\gamma(1 + \gamma)(4\gamma^2 - 1)} R(Z).$$

In the equation above $G_F$ is Fermi’s constant, $A$ the atomic mass number, $E_h$ the Hartree energy and $a_0$ the Bohr radius. $C_{SP}$ and $d_e$ are the effective constant of the scalar $P, T$-odd interaction and the electron electric dipole moment, respectively. Herein the proper coefficient (namely 0.283) in front of $a^2 Z^2$ is used in the numerator [27], instead of the misprinted one (0.375) in [24].

For the relation between $E_{\text{eff}}$ and $W_a$ one obtains then

$$E_{\text{eff}} = -\Omega C_{SP} \frac{M_{EDM} A}{d_e \cdot M_{SPT}} Z W_s,$$

in which the quantum number $\Omega$ of the projection of the electron total angular momentum on the internuclear axis is in the present work always taken equal to 1/2.

It is interesting to note that in experiments with one kind of molecules the scalar $P, T$-odd interaction is indistinguishable from the eEDM effect – they both contribute to the $P, T$-odd electron paramagnetic resonance signal. One can, however, disentangle the contributions by taking data from experiments with different molecules (or molecule and atom) as proposed in [24] for eEDM measurements in Tl and YbF.

Taking into account the above relations one can easily estimate the effective electric field acting on the electron in the ground $^2\Sigma$ state of RaF. The results are given in Table II. The accuracy of such an estimate is not high, but sufficient to identify RaF as promising candidate for eEDM measurements.

Another attractive feature of measurements with Ra nuclei is that there exist also a nuclear mechanism enhancing $P$-odd and $P, T$-odd effects in certain Ra isotopes. According to [30] and [31] the Schiff moment in nuclei possessing octapole deformation is enhanced by about 10 to 100 times. The mechanism is similar to the one in diatomic and chiral molecules: enhancement is reached due to closeness of rotational levels of opposite parity. As a result the estimated Schiff moments in $^{225}$Ra and $^{223}$Ra isotopes are equal to 300 and 400 (in units
TABLE II. Calculated and estimated (in parentheses, absolute value only, from Eq. 2) $W_s$ parameter of the $\mathcal{P}, \mathcal{T}$-odd scalar interaction (in kHz) and the effective field on the electron $|E_{\text{eff}}|$ (in units of $10^{24}$ Hz e$^{-1}$ cm$^{-1}$) for open-shell diatomic molecules. The value of $|E_{\text{eff}}|$ is obtained via Eq. [3] from the numerically calculated $W_s$ parameter, the value in parentheses from the estimated $|W_s|$ value. For comparison, $|E_{\text{eff}}|$ as calculated $ab$ initio previously is provided in square brackets.

| Z     | $|W_s|$/Hz$^a$ | $W_s$/kHz | $|E_{\text{eff}}|$ |
|-------|---------------|-----------|----------------|
| BaF   | $56 \times 10^2$ | -8.5 (12) | 1.3 (1.8) [1.9$^b$] |
| YbF   | 70 $\times 10^2$ | -41 (38)  | 4.4 (4.1) [6.0$^b$] |
| RaF   | 88 $\times 10^3$ | -15 $\times 10^4$ | 11 (9.5) |
| HgH   | 80 $\times 10^3$ | -38 $\times 10^4$ | (19 $\times 10^4$) | 32 (16) |
| CnH   | 112 $\times 10^4$ | -87 $\times 10^5$ | (35 $\times 10^5$) | 746 (300) |

\(\eta 10^8\) e fm$^3$, where \(\eta\) is effective nucleon-nucleon \(\mathcal{P}, \mathcal{T}\)-odd force constant, respectively, whereas for \(^{199}\)Hg for example it is only $-1.4$ (data taken from Ref. [31]).

PRODUCTION OF RAF

Besides the possible routes discussed in Ref. [13], we propose in Ref. [32] to produce neutral RaF via RaF$^+$, which is subsequently neutralised by charge exchange in collision with a suitably chosen collision gas or by interaction with surfaces that provide the adequate work function for an iso-enthalpic electron transfer. RaF$^+$ can in turn be formed in reactive collisions of radium ions with a suitable fluorine containing compound.

CONCLUSION

We demonstrated various special properties of RaF that render it a versatile molecular laboratory for studying a wide range of physical phenomena, from laser cooling to physics beyond the Standard Model. A unique combination of rovibronic and nuclear structure features renders RaF particularly attractive for further experimental study. For the first time the parameter of the scalar $\mathcal{P}, \mathcal{T}$-odd interaction $W_s$ is calculated with the accounting for spin-polarisation for the molecules RaF, HgH and CnH. The authors are grateful to D. DeMille, V. Flambaum, M. Kozlov and S. Hoekstra for discussion.

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