

Laser-cooled RaF as a promising candidate to measure molecular parity violationT. A. Isaev,¹ S. Hoekstra,² and R. Berger¹¹*Clemens-Schöpf Institute, TU Darmstadt, Petersenstrasse 22, D-64287 Darmstadt, Germany*²*KVI, University of Groningen, Zernikelaan 25, NL-9747 AA Groningen, The Netherlands*

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The parameter W_a , which characterizes nuclear-spin-dependent parity violation (PV) in the molecular spin-rotational Hamiltonian, was computed with a quasirelativistic Hartree-Fock approach for radium fluoride (RaF) and found to be one of the largest absolute values predicted so far. The peculiar electronic structure of RaF leads to highly diagonal Franck-Condon matrices between the energetically lowest two electronic states, which qualifies RaF for direct laser cooling. A subset of diatomic molecules with a wide range of internal structures suitable for this cooling technique is also indicated. As trapped cold molecules offer superior coherence times, RaF can be considered promising for high-precision experiments aimed at molecular PV.

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Diatomic radicals containing heavy nuclei are, together with closed-shell chiral molecules with high- Z nuclei [1,2], especially suitable in the search for parity-violation effects, which depend on nuclear spin (see review [3]). Up to now, the only measured nuclear-spin-dependent parity-violating (NSDPV) quantity has been the anapole moment [4,5] of the ^{133}Cs nucleus [6]. Nevertheless, it was concluded that the result of this experiment is in contradiction with previously obtained restrictions on NSDPV constants (see the review [7]), which means that further attempts are needed to determine the NSDPV effects. Currently, an experiment on the measurement of the nuclear anapole moment of barium in the barium fluoride (BaF) molecule using a molecular beam is in preparation at Yale University [8]. Here we propose the use of trapped radium fluoride (RaF) molecules as a promising candidate to probe parity violation, which has never been detected in molecular spectroscopy.

In recent years, a number of techniques have been developed to prepare, control, and cool molecules [9]. A level is now being reached at which these techniques can have a significant impact on precision experiments. Stark deceleration, well suited to slow down and trap diatomic polar molecules, has been developed in the past decade [10–12], and the possibility of laser cooling of molecules has only recently received more attention [13–15], which has led to the first molecular laser-cooling results [16]. By the application of such cooling methods to sensitive molecules, a new generation of precision measurements can be performed.

As we show in this paper, the RaF molecule appears very well suited for laser-cooling methods, because of (i) the highly diagonal Franck-Condon (FC) matrix between the electronic ground state and the energetically lowest electronically excited state and (ii) the facts that (a) the corresponding electronic transition frequency is in the visible region with a reasonable lifetime and (b) isotopes with nuclear-spin quantum number $I = 1/2$ are available. Combined with the high sensitivity of the molecular electronic structure to NSDPV interactions, this makes the RaF molecule a prime candidate for a precision experiment probing molecular parity violation.

An experiment with radioactive molecules requires a specialized facility. At the Kernfysisch Versneller Instituut (KVI) of the University of Groningen, the TRI μ P facility for the production of radioactive isotopes was commissioned in

2007, with the perspective of using these radioactive isotopes in precision experiments to test fundamental symmetries [17]. As the accuracy in a spectroscopic measurement is ultimately limited by the coherence time, there is a clear potential for precision experiments using trapped species. A number of precision experiments using trapped species have been set up, such as Ra^+ to probe parity violation [18] and Ra atoms for electron electric-dipole moment (eEDM) detection [19]. We discuss the production, deceleration, and trapping of RaF molecules further on in this paper.

I. CALCULATION OF THE W_a PARAMETER

Previously [20], we utilized the quasirelativistic two-component zero-order regular approximation (ZORA) to calculate the NSDPV parameter W_a of the effective molecular spin-rotational Hamiltonian in a number of heavy-atom diatomic molecules. The corresponding P -odd contribution to this Hamiltonian reads $W_a k_A (\hat{\lambda} \times \vec{S}_{\text{eff}}) \cdot \vec{I}$, where \vec{S}_{eff} is the effective electron-spin operator, \vec{I} is the nuclear-spin operator, the vector $\hat{\lambda}$ points from the heavy nucleus to the light one, and k_A is the parameter of the heavy nucleus [7], which includes the effect of the nuclear anapole moment and the NSD Z^0 exchange contribution. One may also attempt to absorb the effects from the nuclear-spin-independent Z^0 exchange contribution in k_A , but as this contribution depends, via the hyperfine coupling tensor, also on the specific electronic structure, it may appear more canonical to include this contribution in the electronic-structure parameter W_a . For the time being, however, we have omitted this (supposedly small) additional term.

The results obtained with this approach are at the level of paired generalized Hartree-Fock (paired GHF; for the classification used, see the review [21]) for *off-diagonal* matrix elements (MEs) between the degenerate electronic states (W_a), while *diagonal* MEs (components of the hyperfine coupling tensor) correspond to complex GHF, thereby including spin-polarization effects. The advantage of our approach is that it can be straightforwardly extended to polyatomic molecules. In the case of diatomic molecules with a $^2\Sigma$ ground state, we can obtain reliable estimates of the NSDPV effect together with the hyperfine coupling tensor \mathbf{A} using ZORA. In our calculations, we used a modified version [20,22,23] of the TURBOMOLE code [24,25] with an even-tempered atomic basis set on Ra,

TABLE I. Molecular parameters for the two-component GHF-ZORA description of the electronic ground state $^2\Sigma_{1/2}$ of ^{213}RaF , ^{223}RaF , and ^{225}RaF . The results are given for R_e taken from both the GHF-ZORA ($4.40a_0$) and FS-CCSD ($4.24a_0$) calculations. The parallel and perpendicular components of the hyperfine tensor are given in gigahertz, and W_a is given in kilohertz (with the estimated dependence on the Ra mass number being on the order of a few hertz). To estimate the contribution from spin-polarization effects, the paired GHF values of the hyperfine tensor components are given in parentheses.

R_e (units of a_0)	^{213}RaF		^{223}RaF		^{225}RaF		W_a (kHz)
	A_{\parallel} (GHz)	A_{\perp} (GHz)	A_{\parallel} (GHz)	A_{\perp} (GHz)	A_{\parallel} (GHz)	A_{\perp} (GHz)	
4.40	12.6 (10.6)	12.4 (10.5)	1.86 (1.56)	1.82 (1.56)	-15.1(-12.7)	-14.8(-12.6)	1.36
4.24	12.9 (10.9)	12.6 (10.7)	1.90 (1.60)	1.86 (1.58)	-15.4(-13.0)	-15.1(-12.9)	1.30

a basis set of triple- ζ quality from the TURBOMOLE basis-set library augmented with diffuse p and d functions on the F atom (see supplementary material [26] for basis sets and other parameters of the calculations). A finite spherical Gaussian nucleus model is used, and a ZORA model potential as proposed by van Wüllen [27] with additional damping [28] was applied. The equilibrium distance R_e of the electronic ground state was obtained from complex GHF-ZORA calculations and found to be in good agreement with R_e determined in later four-component (relativistic) Fock-space coupled cluster singles and doubles (FS-CCSD) calculations. As one can see from Table I, the changes for all parameters are within 6% when the R_e value is taken either from FS-CCSD or GHF-ZORA calculations. The computed absolute value of the W_a parameter is in the kilohertz range and thus is one of the largest predicted for diatomic molecules so far. The comparison of W_a for BaF ($W_a = 111$ Hz) with that for RaF indicates a Z^5 dependence of the magnitude of the NSDPV effect. Nevertheless, this is not in conflict with the so-called “ Z^2 rule,” as one has to account also for a relativistic enhancement factor (see the book by Khriplovich [29] for explicit expressions of the corresponding matrix elements), which is about 3 for BaF and about 12 for RaF. We performed systematic studies of NSDPV effects in a series of homologues [e.g., $M\text{H}$ ($M = \text{Zn}, \text{Cd}, \text{Hg}$)], and the results of our study will be presented in a later article.

As Ra nuclei have an even number of protons, measurements of W_a in RaF would ideally complement previous ^{133}Cs experiments on the nuclear anapole moment of nuclei with an odd number of protons. The hyperfine coupling tensor calculated herein for RaF with (and without) accounting for spin-polarization effects is highly isotropic and can be used, once measured, to estimate the quality of our prediction for W_a . We provide hyperfine tensor values for two Ra isotopes with nuclear-spin quantum number $I = 1/2$ (^{225}Ra and ^{213}Ra), which can be produced at KVI (see later in the article). The nuclear Schiff moment of the ^{223}Ra isotope with $I = 3/2$ is considerably enhanced due to octupole deformation [30], so we also provide data on this nucleus.

Besides the high W_a value, there is also another peculiarity which makes RaF very attractive for experimental NSDPV research, namely that this molecule appears well suited for being directly cooled with lasers.

II. FC FACTORS AND DIRECT LASER COOLING OF MOLECULES

One of the major problems in direct laser cooling of molecules is the spontaneous radiative decay into a manifold

of rovibrational states not covered by the cooling cycle. Transitions between rotational states are driven by selection rules for vector operators and can be reduced to the two-level case [14], but depopulation of vibrational levels during cooling cycles is the obstacle. In Ref. [13], several molecules were proposed which have highly diagonal overlapping matrices between vibrational eigenfunctions of the ground and the first excited electronic states (in terms of the molecular spectroscopy—highly diagonal FC matrices). For 10^4 – 10^5 cooling cycles, the probability that the molecule will stay inside the cooling loop has to be greater than 0.9999, with the *fourth digit being significant*. In practice, this means that one has to know FC factors with an accuracy of 0.01%, which is extremely challenging to achieve in modern calculations (although FC factors can, in principle, be measured with high accuracy). Thus *predictions* of FC factors with the required experimental accuracy appear practically impossible.

Nevertheless, one can try to narrow down the number of candidate systems for direct cooling with lasers based on peculiarities of the molecular electronic structure, which renders certain molecules promising. We have analyzed the electronic structure of diatomic molecules with one electron over closed shells. Such molecules have large magnetic moments (in comparison with the closed-shell systems), which makes them suitable for magnetic trapping. More detailed considerations will be made in a later article; here we just give a short summary. Highly diagonal FC matrices should be expected when the unpaired electron is making transitions between orbitals that do not contribute to the bonding. Such one-electron wave functions can be of the following type: (1) “Electron in lone orbital.” This situation is well-known in theoretical chemistry when, as a result of sp^n hybridization, for example, an unpaired electron is directed out of the bonding region. This takes place, for example, in the electronic ground state of $M\text{F}$ and $M\text{H}$, where M belongs to the group of alkaline earth metals (Mg to Ra; see the article [31] for some examples). Two molecules from this series were already used to indicate the perspectives of direct molecular cooling, namely CaH in Ref. [13] and SrF in Ref. [14,16]. (2) “Atomlike electron in molecule.” In this case, the outer electron is, due to various reasons (symmetry as a rule), located in a highly symmetrical state, which has an almost atomic nature. Such a situation happens, for example, in HI^+ [32], where the unpaired electron resides in an orbital which is mainly of atomic $p_{3/2}$ character centered on iodine. In isoelectronic neutral molecules (such as TeH), the situation is expected to be the same. (3) In heavy-atom compounds, the valence electron orbital is often quite diffuse, thus the maximum density of the unpaired

electron is located farther away from the molecular core than in lighter homologues. Thus among all possible molecules, those with heavier nuclei appear promising.

The heavy-atom molecules RaF, HgH, HgF, etc., which should belong to the first class, and HI⁺, PoH, TeH, etc., which should belong to the second class, are expected to have highly diagonal FC matrices. Thus they appear, in principle, to be highly suitable candidates for direct cooling of molecules. Unfortunately, the molecules belonging to the second class are not particularly suitable for NSDPV experiments, as the unpaired valence electron is in an orbital with high total angular momentum and does not have noticeable spin density in the vicinity of the heavy nucleus. As to the first class, the molecules HgH and HgF have (as RaF) a $^2\Sigma$ ground state and, according to our estimates, even higher W_a values (for HgH it is 3.3 kHz, although we emphasize again that spin polarization and other electron correlation effects are not accounted for in our W_a estimates, while these effects may well be important). The excitation energy of the first excited state in some of these molecules, however, is in the ultraviolet region (407 nm for HgH and 256 nm for HgF) [33]. At 256 nm, it might prove difficult to produce sufficiently intense laser light. Moreover, as indicated by preliminary spectroscopic data [34] and by earlier explicit theoretical investigations [35] beyond our present general considerations, both HgH and HgF may not be suitable for direct laser cooling due to relatively large differences in equilibrium structures for the ground and first excited electronic states. In the series MF , on the other hand, where M belongs to the group of alkaline earth metals, the excitation energies from the ground to first excited electronic states are in the visible region, so one can expect a similar situation in RaF. This wavelength region is directly accessible using diode lasers.

To substantiate the previous considerations, we performed exemplary four-component FS-CCSD calculations of the six lowest-lying states of RaF using the DIRAC08 package [36]. The details of the FS-CCSD approach are given in the review [37]. Electrons of the $6s, 6p, 7s$ shells of Ra and $2s, 2p$ of F are correlated; the basis sets and other computational parameters can be located in the supplementary material.

The two energetically lowest-lying electronic states are identified as $^2\Sigma_{1/2}$ (ground state) and $^2\Pi_{1/2}$ (first excited state), which proves the similarity of the *valence* electronic structure of RaF with its lighter homologue BaF. Then the points calculated in the interval $3.5a_0$ to $7.0a_0$ were fitted by a Morse potential (the points and fitting curves are given as a figure in the supplementary material), and spectroscopic parameters together with the corresponding FC factors were determined. The FC factors were calculated by the MATHEMATICA script for FC factor calculation between vibrational Morse oscillator states taken from Ref. [38]. The results obtained are presented in Table II.

The laser-cooling transition [$^2\Pi_{1/2}(v' = 0) \leftarrow ^2\Sigma_{1/2}(v = 0)$] is found to lie around 710 nm, and an upper-state lifetime on the order of ~ 25 ns is expected. With these parameters, the capture range for optical molasses is ~ 5 m/s, and the Doppler limit temperature is ~ 150 μ K. If a precooled sample of molecules can be created, as is described in the next section, only a few thousand photons would have to be scattered per molecule to reach this temperature. At these temperatures,

TABLE II. Estimated molecular spectroscopic parameters for the electronic ground state $^2\Sigma_{1/2}$ and the first electronically excited $^2\Pi_{1/2}$ state from FS-CCSD calculations of ^{226}RaF . The dissociation energy $hc\tilde{D}$ was obtained as the difference between total energies of the states at the equilibrium distance R_e and at $9.0a_0$ without attempting to correct for basis-set superposition errors. Fitting parameters of the Morse potential with the corresponding standard errors can be found in the supplementary material. The parameter $\tilde{\omega}_e$ refers to the harmonic vibrational wave number. We emphasize that the accuracy of the determination of the parameters is lower (especially for \tilde{D} and \tilde{T}_e) than the number of digits reported. Nevertheless, we give the results with higher digital precision to provide reference points for future calculations.

	R_e (units of a_0)	$\tilde{\omega}_e$ (cm^{-1})	\tilde{D}_e (cm^{-1})	\tilde{T}_e (cm^{-1})
$^2\Sigma_{1/2}$	4.24	428	32104	
$^2\Pi_{1/2}$	4.24	432	31302	14012

only a very small volume in the trap is occupied, opening the possibility to perform precision measurements using the trapped molecules.

The sum of the FC factors for the ground vibrational state of the $^2\Pi_{1/2}$ state and three vibrational states of the $^2\Sigma_{1/2}$ state is equal to 0.9999, with four digits after a decimal being stable with respect to variations of the fitting parameters of the Morse potential (see supplementary materials for details). We emphasize here that high *digital* precision in calculations of FC factors does not equate to a high accuracy of the spectroscopic constants calculations. A reliable estimate of the sum of FC factors which can be used for practical purposes is expected to have two digits after a decimal point. Nevertheless, *both* numerical results and arguments from electronic-structure theory provide, in our opinion, good reasons for considering RaF for measurements of the NSDPV effect and for direct laser cooling.

III. PROPOSED MEASUREMENT STRATEGY AND SENSITIVITY TO NSDPV SIGNAL

The W_a parameter can be obtained in a diatomic molecule by a measurement of the parity-violating coupling between hyperfine-rotational levels of opposite parity. An experimental procedure to do so in a molecular beam was proposed in Ref. [8], where tuning of the close-lying spin-rotational levels of opposite parity to near-degeneracy due to the Zeeman effect was used to increase the P -odd asymmetry in the measured signal.

The accuracy in the determination of W_a that can be reached in such an experiment is proportional to the count rate of the molecular signal (dN/dt), the interaction (coherence) time (T), and the total measurement time (τ) as $\delta W_a \sim 1/(T\sqrt{\tau dN/dt})$.

In a molecular-beam experiment, with an interaction region of 5 cm and a molecular-beam velocity of 500 m/s, the interaction time is on the order of 100 μ s. It has been demonstrated that cold molecules can be trapped for at least a number of seconds [39,40]. If a coherence time of 1 s could be reached, the gain compared to a molecular-beam experiment would be four orders of magnitude. This is assuming a

comparable number of molecules. It is clear that part of this gain is lost as the number of trapped molecules will probably be low. To assess the final accuracy that can be reached in such an experiment, therefore, we have to estimate the number of molecules that can be trapped. Before doing so, we point out that, due to the square-root scaling of the accuracy with the number of molecules, even if we were to lose a factor of 10^8 in the number of molecules compared to a molecular-beam experiment (which has an estimated count rate of 50 s^{-1} [8]), we would still be able to get a 10% accuracy determination of the W_a parameter within a week of measurement time. This means that even an experiment using a single trapped molecule could outperform a molecular-beam experiment. The high FC overlap in the RaF molecule should allow for the detection of multiple photons for each trapped molecule, which helps to reach a high detection efficiency when using only a few trapped molecules. Furthermore, compared to the BaF molecule, the high W_a parameter of the RaF molecule will lead to a larger signal for similar statistics.

The two radium isotopes that are most suitable are ^{213}Ra and ^{225}Ra , with lifetimes of 164 s and 14.9 days, respectively. Both isotopes have a nuclear spin $I = 1/2$, which reduces the number of lasers required for laser cooling. The ^{213}Ra isotope has been successfully produced and used in experiments at the KVI [41], whereas ^{225}Ra is best obtained from a ^{229}Th source.

The radium ions from the cyclotron can be implanted in a solid AlF_3 target. RaF molecules can be produced from this target by laser ablation. Alternatively, a RaF_2 target [42] could perhaps be used. The RaF molecules could then be brought in the rovibrational ground state by combining the laser ablation with a supersonic expansion. This is a standard technique to prepare internally cold molecular beams. The bottleneck in this approach, when starting with a limited amount of source material, is the fraction of the evaporated molecules that can be captured in the supersonic beam. In laser ablation, up to 10^{14} particles per pulse are evaporated [43]. By laser ablation of AlF_3 with Yb, packets of about 10^6 ground-state YbF molecules per shot through the skimmer have been produced [44], indicating an efficiency on the order of only 10^{-8} for the transfer from the solid target to a cold molecular beam. Alternatively, the ablation can be performed in a cold cell filled with helium buffer gas, and the cold molecules can be directly captured by a magnetic trap [45]. For optimal trapping, the buffer gas has to be removed quickly [46]. A promising number of 10^{12} YbF molecules, produced in a single laser ablation shot, have been reported [47]. How large a fraction of these can be trapped remains to be seen. But as pointed out, due to the large increase of the interaction time, even with very few trapped molecules a competitive experiment could be done.

The final sensitivity that can be reached in a Stark-interference measurement using trapped molecules requires further careful study of many systematic effects, which is beyond the scope of this article. It is clear, however, that lowering the temperature of the sample of trapped molecules will reduce the influence of the trapping potential on the energy levels of the molecules. This is why we have pointed out the potential for laser cooling of RaF molecules. It might prove to be difficult to cool a gas of room-temperature molecules using just laser-cooling methods. The use of precooling by a cold buffer gas simplifies the task tremendously by already internally cooling the molecules, and it greatly reduces the amount of photons that have to be scattered in order to reach the Doppler temperature limit. This is a big advantage, especially if the cooling cycle is not completely closed.

Concluding this assessment of the experimental challenges and possibilities, a sample of cold radioactive molecules can be obtained to perform a competitive measurement of PV effects in heavy diatomic molecules, even though it certainly is a challenging experimental task. In a first measurement, the hyperfine structure of the RaF molecules can be measured by spectroscopy of the ablated molecules, which can be used to benchmark our calculations. As experimental efforts proceed toward trapping of the molecules, we point out that an investigation of many of the systematic effects can be performed using stable (but less sensitive to PV) molecules. In the end, however, a large W_a parameter is the key to *both* an accurate determination of NSDPV effects and optimal control over systematic effects.

To conclude, we have investigated the suitability of the RaF molecule to probe parity violation, which has not been detected as yet in molecules. Explicit *ab initio* calculations of the NSDPV parameter W_a and FC factors for transitions between the electronic ground state and the lowest doublet excited state indicate that this open-shell molecule is a promising candidate for direct laser cooling and (subsequent) measurement of the nuclear anapole moment. We have also discussed possible approaches to creation, trapping, and cooling of RaF molecules. RaF appears to be a valuable addition to the variety of molecules that can be used to probe PV, providing complementary insight into the NSDPV effects.

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