Radium compounds have attracted recently considerable attention due to both development of experimental techniques for high-precision laser spectroscopy of molecules with short-lived nuclei and amenability of certain radium compounds for direct cooling with lasers. Currently, radium monofluoride (RaF) is one of the most studied molecules among the radium compounds, both theoretically and recently also experimentally. Complementary studies of further diatomic radium derivatives
are highly desired to assess the influence of chemical substitution on diverse molecular parameters, especially on those connected with laser cooling, such as vibronic transition probabilities, and those related to violations of fundamental symmetries. In this article high-precision \textit{ab initio} studies of electronic and vibronic levels of diatomic radium monochloride (RaCl) are presented. Recently developed approaches for treating electronic correlation with Fock-space coupled cluster methods are applied for this purpose. Theoretical results are compared to an early experimental investigation by Lagerqvist and used to partially reassign the experimentally observed transitions and molecular electronic levels of RaCl. Effective constants of $P$-odd hyperfine interaction $W_a$ and $P$, $T$-odd scalar-pseudoscalar nucleus-electron interaction $W_s$ in the ground electronic state of RaCl are estimated within the framework of a quasirelativistic Zeroth-Order Regular Approximation approach and compared to parameters in RaF and RaOH.

I. INTRODUCTION

Recently, a new technique has been developed that allows to perform high-precision laser-spectroscopic studies of molecules with short-lived nuclei [1]. The first spectroscopic information on radium monofluoride (RaF) molecule was obtained with this method, including that of isotopologues with lifetime as short as a few days. These studies have opened an avenue for both fundamental and practical investigations with radioactive compounds on numerous radioactive-ion-beam facilities around the world. The experimental scheme heavily relies on information from electronic structure modeling for the corresponding compounds, and in this connection calculations of the electronic structure of RaX systems, where X is a group 16 or 17 element of the Periodic Table attract considerable attention: In such compounds one could expect considerable enhancement of $P$- and $T$-odd effects, including those connected with nuclear spin (see [2–5] and references therein) as well as the existence of highly closed optical cycling loops, which make such molecules amenable for direct laser cooling [4]. Thus, radium compounds are especially attractive for experi-
mental search for signatures of new physics, including $P$- and $T$-odd effects. The radium monochloride molecule (RaCl) is of special interest as it allows to observe the influence of halogen substitution in RaX compounds on various molecular parameters, particularly on those connected with laser cooling, such as Franck–Condon (FC) factors and oscillator strengths, as well as on $P$- and $T$-odd effects. The precursor material radium dichloride is more readily available on the bulk level, which is important for future off-line spectroscopic studies. Moreover, early experimental data on optical spectra of RaCl containing the long-lived isotope $^{226}$Ra exist, which date back to 1953 \[6\] and motivate the present study (during the course of our work on the present manuscript, we became aware of another theoretical study on RaCl \[7\] triggered by discussions of T. Isaev with the authors of that manuscript). As RaF, the RaCl molecule is also an excellent object to test modern methods of relativistic electronic structure calculations. To study ground and excited electronic states of RaCl with high accuracy, we employ the Fock-space relativistic coupled cluster method (\[8\] and references therein). Transition probabilities and lifetimes of the excited states are computed within the finite-field technique \[9, 10\], successfully applied earlier to a number of heavy-atom compounds \[11, 12\]. Additionally, we estimate effective constants of $P$-odd hyperfine interaction $W_a$ and $P, T$-odd scalar electron-nucleus interaction $W_s$ (see \[2\] for definition of the constants) of the ground electronic $^2\Sigma_{1/2}$ state of RaCl in the framework of Zeroth-Order-Regular-Approximation combined with Generalized Hartree-Fock or Generalized Kohn-Sham approach (ZORA/GHF and ZORA/GKS respectively).

II. COMPUTATIONAL DETAILS

a. Excited state calculations. Accurate \textit{ab initio} evaluation of transition energies in RaCl implies an adequate description of relativistic effects, including those beyond the conventional Dirac–Coulomb model. The non-negligible effect of non-Coulombian (Breit) electron-electron interactions on the lowest $(7s - 6d)$ excitation energies in the atomic Ra$^+$ ion had been demonstrated in \[13\].

Many modern relativistic all-electron codes for electron correlation calculations in molecules, however, do not account for the Breit interaction. Furthermore, the secondary relativistic expansion and destabilization of high-angular-momentum one-electron states of Ra leads to the necessity to correlate, in addition to the valence and eight subvalence (6sp)
electrons, also the electrons associated with the 5d-shell. Additional difficulties stem from a
very slow convergence of 6d-state correlation energies for Ra\(^+\) with the extension of orbital
basis sets; preliminary estimates have shown that the basis set should preferably include
functions with orbital angular momentum quantum numbers \(l\) of up to 6 (\(i\)-functions).

Taking into account above-mentioned challenges we are using in the present work the relativistic
electronic structure model defined by accurate two-component pseudopotentials of “small”
atomic cores derived from the valence-shell solutions of the atomic Dirac–Fock–Breit equa-
tions. Implicitly incorporating the bulk of Breit interaction effects and leaving the electrons
of outer core shells for explicit correlation treatment, this model also offers the possibility
of using sufficiently large and flexible contracted Gaussian basis sets.

In the present study, the pseudopotentials \([14, 15]\) replaced the shells with the principal
quantum number \(n \leq 4\) for Ra and the 1s-shell for Cl. The basis set for Ra comprised a set
of primitive Gaussians \((10s\,9p\,9d\,7f)\), loosely based on the diffuse part of the primitive function
set from Ref. \([16]\), and the contracted Gaussians \((7g\,6h\,5i)/[4g\,3h\,2i]\) obtained as averaged
atomic natural orbitals in scalar-relativistic calculations on low-lying electronic states of
Ra and Ra\(^+\). The \((10s\,12p\,4d\,3f\,2g)/[6s\,7p\,4d\,3f\,2g]\) chlorine basis was a straightforward
adaptation of the aug-cc-pVQZ set \([17]\) to the use with the pseudopotential, extended by
the additional single set of contracted \(p\)-functions \((2p_{3/2} - 2p_{1/2})\) to improve the description
of spin-orbit splittings. Exponential parameters and linear expansion coefficients for the
contracted basis sets can be found on the website \([15]\) and are given in the Supplementary
materials.

Correlation calculations were performed using the FS RCC method \([8]\). Molecular
(pseudo) spinors were generated by solving the SCF equations for the closed-shell ground
state of RaCl\(^+\) which was used as Fermi vacuum state. The ground and low-lying excited
states of neutral RaCl thus corresponded to the 0h1p sector of the Fock space. The cluster
operator expansion comprised only single and double excitations. 27 electrons (20 electrons
of Ra, including those of subvalence 5d6sp shells, and 7 valence electrons of Cl) were corre-
lated whereas the spinors corresponding to the 5sp shells Ra and 2sp shells Cl were frozen
after the Hartree–Fock step. In most calculations the model space in the target 0h1p sector
was defined by 9 Kramers pairs of “active” spinors.

To reduce systematic internuclear-distance-dependent errors in the energy values arising
from the neglect of higher cluster amplitudes and the basis set superposition (BSSE) \([18]\) the
potential energy curves for the excited states were constructed by adding the FS RCC vertical excitation energies calculated as functions of the internuclear distance, to the ground state potential recomputed with perturbative account for the contribution from triple excitations (RCCSD(T) scheme) and with counterpoise corrections of the BSSE. The calculations were performed for internuclear separations $R$ in the range $4.6 \ a_0 \leq R \leq 6.5 \ a_0$, where the validity of the chosen electronic structure model (restriction to the single Fock space sector $0h1p$) for the low-lying states $(1 - 5) \ 1/2$, $(1 - 3) \ 3/2$, and $(1) \ 5/2$ was not in doubt; at the same time the chosen coordinate range for the potential energy curves was sufficiently large for highly accurate numerical evaluation of wavefunctions and energies of $4-5$ lowest vibrational levels for each of these states.

In order to get insight into the impact of spin-dependent relativistic effects on the composition of the excited state wavefunctions, we computed the scalar relativistic counterparts of the states under study via switching off the spin-orbit parts of the pseudopotential and projected these states onto the model-space parts of fully relativistic states (cf. [19]).

Matrix elements of the electric transition dipole moment between the low-lying electronic states were evaluated using the finite-field technique [9–11]. In contrast to total energies, the finite-field transition dipole estimates are significantly improved upon extension of the model space [10], so here we used a larger model space corresponding to $19$ Kramers pairs of active spinors. Numerical instabilities which appeared for this extended model space were eliminated by applying small “dynamic” shifts of FS RCC energy denominators [19] in the target sector (shift amplitudes $-0.05 \ E_h$ and $-0.10 \ E_h$ for single and double excitations, respectively, and the attenuation parameter $m = 3$, see Eq. (4) in Ref. [19]).

The Kramers-restricted SCF and single-reference RCCSD(T) ground state calculations were performed with the DIRAC program suite [20]. For FS RCC calculations we employed the EXP-T program recently developed by some of the authors of the present work (A.O., A.Z., and E.E.) [21, 22]. Transformed molecular integrals were calculated with the help of the DIRAC 18 program suite and then imported to EXP-T.

Vibrational wavefunctions and energy levels as well as FC factors were evaluated with the help of the program VIBROT [23].

b. Calculations of $W_a$ and $W_s$ constants. The $P$-odd nuclear spin-dependent and $P, T$-odd scalar electron-nucleus contributions for the given nucleus $A$ (in our case the Ra nucleus) in paramagnetic diatomic molecules are described by the following terms of the effective
molecular Hamiltonian [2] [24]:

\[
W_a k_A \left[ \vec{\lambda} \times \vec{S}^{\text{eff}} \right] \cdot \vec{I} + W_s k_{SP} \vec{\lambda} \cdot \vec{S}^{\text{eff}},
\]

(1)

where \( \vec{\lambda} \) is the unit vector directed from Ra to Cl, \( \vec{S}^{\text{eff}} \) is the effective electronic spin and \( W_a \) and \( W_s \) are parameters, which have to be deduced from electronic structure calculations. The physical meaning of the \( W_a \) parameter is \( \mathcal{P} \)-odd hyperfine coupling constant [25, 26], while \( W_s \) can be related to the parameters of \( \mathcal{P}, \mathcal{T} \)-odd electron paramagnetic resonance. The computation scheme of \( \mathcal{P} \)-odd and \( \mathcal{P}, \mathcal{T} \)-odd parameters is analogous to that used in [26] [27]. We used for Ra basis set of uncontracted Gaussian with the exponent coefficients composed in the even-tempered manner as in [26]. For Cl basis set of triple-zeta quality augmented with polarisation \( d \)-functions from tm2c basis set library (TZz) is used (see Supplementary for explicit basis set exponents). The nuclear density was modelled by a spherical Gaussian distribution \( \rho(R) = \rho_0 e^{-\frac{3}{2}\xi R^2} \), where \( \xi \) is the mean root square radius of the corresponding nucleus computed according to the empirical formula

\[
\xi = (0.836A^{1/3} + 0.57) \text{ fm} = (1.5798A^{1/3} + 1.077) \times 10^{-5} \text{ a}_0,
\]

where \( A \) is taken equal to be 226 for Ra. A modified version [27] [30] of the program package TURBOMOLE [31] was used for the generalised Hartree–Fock (GHF) or generalised Kohn–Sham (GKS) calculations. The value of \( \mathcal{P} \)-odd and \( \mathcal{P}, \mathcal{T} \)-odd parameters are calculated at equilibrium internuclear distance obtained in structure energy-minimisations performed by TURBOMOLE using 68-electron Stuttgartt effective core potential on Ra with TZVP basis set on Ra [9s,9p,5d,3f] and TZP basis set on Cl [9s,5p,1d]. The optimised \( R_e \) value is 5.361 \( \text{ a}_0 \) which is quite close to the \( R_e \) from RCCSD(T) calculations (5.271 \( \text{ a}_0 \)). The parameter \( |W_a| \) was calculated according to the Eq. (3) from [27], and the parameter \( W_s \) according to the Eqs. (2) – (4) from [5] (we note that due to a typo the \( \rho_A(\vec{r}) \) member was omitted in expression (2) in [5]). We have neglected the contributions from the relatively light nuclei of Cl to the considered molecular \( \mathcal{P} \)-odd and \( \mathcal{P}, \mathcal{T} \)-odd properties, due to the strong dependence of these effects on the nuclear charge (see e.g. [27] and references therein). We note that in the direct application of the present complex GHF/GKS approach only the absolute value of \( W_a \) is immediately accessible, while for \( W_s \) the sign is determined directly in the calculations.
III. RESULTS AND DISCUSSION

The resulting potential energy functions are presented in Fig. 1 and the derived values for the main molecular constants of RaCl along with the corresponding spectroscopic data from Ref. [6] and estimated transition moments to the ground states are listed in Table I. The low-lying excited states, $(2 - 3) 1/2$, $(1 - 2) 3/2$, and $(1) 5/2$, having very similar shapes of interatomic potentials, form a rather tight group which can be naturally associated with $^2D_J$-states of Ra$^+$ perturbed by the interaction with the chlorine anion. The parameters of two states with bright transitions from the ground one, namely, the second state with $\Omega = 3/2$ and third state with $\Omega = 1/2$, are in excellent agreement with those of the experimentally observed states $C$ and $C'$ [6]. The small deviations of the computed $T_e$ values from their experimental counterparts (+139 cm$^{-1}$ for and +154 cm$^{-1}$ respectively) correlate with the slight (210–220 cm$^{-1}$) overestimation of $7s - 6d$ excitation energies in the free Ra$^+$ atomic ion within the present electronic structure model.

The present model provides directly the RCCSD(T) estimate for the RaCl ground-state dissociation energy to the ionic fragments, Ra$^+$ ($7s^2S_{1/2}$) and Cl$^-$ ($1S_0$), 47 680 cm$^{-1}$. Combining this estimate with the accurate experimental ionization energy of atomic Ra, 42 573 cm$^{-1}$ [32] and electron affinity of chlorine, 29 139 cm$^{-1}$ [33], one readily obtains the RaCl adiabatic dissociation energy $D_e = 34 246$ cm$^{-1}$ (ca. 4.25 eV). The FS RCCD calculation on Ra ionization potential (with the vacuum state redefined as $7s^2 1S_0$) and chlorine electron affinity yields the values 42 913 cm$^{-1}$ and 29 477 cm$^{-1}$, respectively, which can be used to evaluate the RaCl ($X 1/2$) dissociation energy to the lowest-energy channel without any reference to empirical data ($D_e = 34 244$ cm$^{-1}$).

Making use of the analogy between RaCl and the monochlorides of lighter group II elements, Lagerqvist had identified the $C, C'$ states with the components of the spin–orbit-split $^2\Pi$ manifold [6]. The splitting of 604.4 cm$^{-1}$ between the two levels observed in experiment would, indeed, be essentially consistent with the expected spin–orbit splitting in the $C$ state of RaCl. But this level is expected — and also computationally found — at higher and not lower energies than the corresponding level in BaCl: It correlates with the $7p$ level of Ra$^+$, and the $np$ level in the alkaline earth monocations is known to drop in the sequence from Be$^+$ to Ba$^+$, but raises again for Ra$^+$. The $\Lambda–S$ coupling scheme is also partially broken for RaCl. The separations between the scalar relativistic excited $^2\Delta, ^2\Pi$, and $^2\Sigma$...
Figure 1. Calculated potential energy functions for the low-lying electronic states of RaCl. Bold lines correspond to the supposed counterparts of the experimentally observed states $X$, $C$, and $C'$. 
Table I. Molecular constants, squared electric dipole transition moments for transition to the ground state \(|d|^2\) and the composition of the model wavefunctions in terms of their scalar relativistic counterparts at \(R_e(X)\) for low-lying electronic states of RaCl.

| \(T_e\), cm\(^{-1}\) | \(R_e\), Å | \(\omega_e\), cm\(^{-1}\) | \(|d|^2\), a.u. | Composition |
|------------------|---------|------------------|-----------------|-----------------|
| \(X(1)\frac{1}{2}\) | 0 | 2.789 | 258.5 | 252.5 | 100\% \(^2\Sigma\) |
| (2)\(1/2\) | 12827 | 2.792 | 259.0 | 253.0 | 4.62 | 26\% \(^2\Sigma\) + 74\% \(^2\Pi\) |
| (1)\(3/2\) | 13487 | 2.800 | 253.9 | 248.0 | 0.21 | 8\% \(^2\Pi\) + 92\% \(^2\Delta\) |
| (1)\(5/2\) | 14454 | 2.794 | 256.3 | 250.3 | 0 | 100\% \(^2\Delta\) |
| (2)\(3/2\) | 14921 | 2.793 | 257.2 | 251.2 | 4.03 | 92\% \(^2\Pi\) + 8\% \(^2\Delta\) |
| (3)\(1/2\) | 15541 | 2.800 | 256.6 | 250.6 | 3.33 | 74\% \(^2\Sigma\) + 26\% \(^2\Pi\) |
| (4)\(1/2\) | 21991 | 2.807 | 258.0 | 251.9 | 2.16 | 99\% \(^2\Pi\) |
| (3)\(3/2\) | 22758 | 2.789 | 265.6 | 259.4 | 2.43 | 100\% \(^2\Pi\) |
| (5)\(1/2\) | 26852 | 2.718 | 274.9 | 268.3 | 0.18 | 99\% \(^2\Sigma\) |

\(\text{RaCl}^+\)

\(\tilde{X}, 0^+\) | 42168 | 2.672 | 294.9 | 287.7 |

terms in the vicinity of equilibrium are about 140 and 800 cm\(^{-1}\), respectively, being much smaller than the spin-orbit splitting of the \(^2D\) level in \(\text{Ra}^+\) (1659 cm\(^{-1}\)) characterizing the intensity of spin-dependent interactions within this group of states. The analysis of the model-space wavefunctions confirms the domination of \(^2\Pi\)-like component in the supposed \(C\) state, (2) \(3/2\), whereas the supposed \(C'\) state, (3) \(1/2\), is a \(^2\Sigma\) - \(^2\Pi\) admixture with a predominance of \(^2\Sigma\) (see the last column of Table I).

We made an attempt to reanalyse the list of transitions reported by Lagerqvist, assuming that the band heads reported as Q1 and Q2 in Lagerqvists work stem from independent electronic states rather than the spin-orbit split \(^2\Pi\) level. The corresponding molecular constants are given in Table II as reanalysis 1. Reanalysis 2 takes additionally into account that \(^{35}\text{Cl}\) and \(^{37}\text{Cl}\) have a natural abundance ratio of approximately 3:1. For the \(\Delta \nu = 0\) branch, one would not expect to observe the difference between isotopic species in a
Table II. Molecular constants for low-lying electronic states of RaCl according to [6] and our re-analysis of experimental data.

| State | $T_e$, cm$^{-1}$ | $\omega_e$, cm$^{-1}$ |
|-------|-----------------|---------------------|
| $^{226}\text{Ra}^{35}\text{Cl}$ | 256.2$^*$ | 
| $^{226}\text{Ra}^{37}\text{Cl}$ | 256.48(14)$^*$ | 
| $^{226}\text{Ra}^{37}\text{Cl}$ | 262.45(16) | 
| $X$, exptl [6] | 0 | 256.2$^*$ |
| $X$, exptl, re-analysis 1$^†$ | 0 | 256.48(14)$^*$ |
| $X$, exptl, re-analysis 2$^†$ | 0 | 262.45(16) |
| $C$, exptl [6] | 14782.1 | 253.8$^*$ |
| $C$, exptl, re-analysis 1$^†$ | 14786.57(11) | 254.01(14)$^*$ |
| $C$, exptl, re-analysis 2$^†$ | 14786.57(12) | 259.98(16) |
| $C'$, exptl [6] | 15386.5 | 252.9$^*$ |
| $C'$, exptl, re-analysis 1$^†$ | 15390.75(10) | 253.18(12)$^*$ |
| $C'$, exptl, re-analysis 2$^†$ | 15390.73(11) | 259.15(14) |

$^*$) Unknown isotopologue  $^†$) Additional parameters from re-analysis 1: $\omega_e x_e$/cm$^{-1}$ for states $X$, $C$ and $C'$: 0.732(12), 0.731(12), 0.744(11); Additional parameters from re-analysis 2: $\omega_e x_e$/cm$^{-1}$ for states $X$, $C$ and $C'$: 0.734(19), 0.733(19), 0.746(18).

measurements with a resolution of 0.01 Å or less. But in the $\Delta \nu = -1$ branch, one would expect to distinguish between the two isotopologues due to the lower abundance of $^{37}$Cl. As only band head positions, but not the intensities were reported by Lagerqvist, one can only tentatively assume that some of the transitions reported correspond to the $^{37}$Cl containing RaCl isotopologue. In reanalysis 2, the first three transition were assumed to belong to $^{226}\text{Ra}^{37}\text{Cl}$, and the following transitions are assumed to be dominated by $^{226}\text{Ra}^{35}\text{Cl}$, which leads to a relabeling of the vibrational quantum number. The constants resulting for the latter isotopologue are given in Table II.

Lagerqvist mentioned already in his early analysis that the Franck–Condon parabola is very narrow for RaCl, which is a prerequisite for laser-coolability. In accordance with the experimental finding, the potential curves of all states of the group under discussion are nearly parallel to that of the ground state; the equilibrium internuclear separation and bond
Table III. Sums of the FC factors for transitions from the lowest \( v' = 0 \) vibrational level of excited states to several vibrational levels \( v \) of the ground electronic state, \( \sum_{i=0}^{n} | \langle v' = 0 | v = i \rangle |^2 \), for \(^{226}\text{Ra}^{35}\text{Cl}\). The corresponding values for \(^{226}\text{Ra}^{37}\text{Cl}\) are nearly the same.

| Initial state | \( n = 0 \) | \( n = 1 \) | \( n = 2 \) |
|--------------|-------------|-------------|-------------|
| (2) 1/2      | 0.998516    | 0.999995    | 1.000000    |
| (1) 3/2      | 0.983494    | 0.999911    | 1.000000    |
| \( C \) (2) 3/2 | 0.997818    | 0.999999    | 1.000000    |
| \( C' \) (3) 1/2 | 0.983924    | 0.999968    | 1.000000    |

strength remain almost unchanged upon electronic excitation. This indicates the possibility for (quasi)closed optical cycles involving these states. We calculated the sums of three largest FC-factors for decay from the lowest \( v' = 0 \) vibrational level of \( (2) 1/2 \), \( (1) 3/2 \), \( (2) 3/2 \), and \( (3) 1/2 \) to the lowest vibrational levels of the ground state. The results (Table III) indicate that at least for the lowest excited state \( (2) 1/2 \) the effective cooling cycle could be built with at most three lasers (one basic laser on \( 0' - 0 \) transition and two repumpers on \( 0' - 1 \) and \( 0' - 2 \)).

The closeness of optical cycles involving higher-lying excited states can be destroyed by spontaneous radiative transitions and internal conversion to lower excited states. The radiative branching rates derived from FS RCC electric transition dipole moments and energies (Table IV) show that the relative probabilities of the decay of the \( (1) 3/2 \), \( (2) 3/2 \), and \( (3) 1/2 \) states to lower excited states are rather small (about \( 10^{-3} \) for the former and \( 10^{-4} \) for two latter states). Moreover, due to the quasidiagonality of FC matrices for deexcitations of all states belonging to the manifold under discussion, the transition to some “intermediate” state should hardly break the cycle: with high probability the radiative decay of such state will still lead to one of the lowest vibrational levels of the ground state. Thus not only the lowest-energy excitation to the \( (2) 1/2 \) state, but also the next three electric dipole-allowed excitations (including those to the experimentally observed \( C \) and \( C' \) states) can be considered as prospective candidates for implementing efficient cooling optical cycles.

The origin of the parallelism of potential curves can be readily interpreted in the frames of
Table IV. Estimates of relative spontaneous radiative decay branching ratios for several excited states of RaCl.

| Initial state | Final states | Branching ratios |
|---------------|--------------|------------------|
| (1)3/2        | \( \rightarrow X : \rightarrow (2)1/2 \) | 1 : 1.2 \cdot 10^{-3} |
| (2)3/2        | \( \rightarrow X : \rightarrow (2)1/2 : \rightarrow (1)3/2 : \rightarrow (1)5/2 \) | 1 : 1.3 \cdot 10^{-5} : 2.5 \cdot 10^{-5} : 2.3 \cdot 10^{-5} |
| (3)1/2        | \( \rightarrow X : \rightarrow (2)1/2 : \rightarrow (1)3/2 : \rightarrow (2)3/2 \) | 1 : 3.9 \cdot 10^{-4} : 2.7 \cdot 10^{-4} : 1.0 \cdot 10^{-5} |

a simple one-electron picture [4]. Note that the model-space projection of any FS RCC wavefunctions in the 0h1p sector is immediately and exactly converted to a single-determinant form ("one-electron-over-closed-shell") by an appropriate transformation of active spinors. Excitations from ground to low-lying excited electronic states are therefore dominated by the promotion of the unpaired valence electron to some higher-lying spinor. Fig. 2 provides the graphical representation of these “pseudonatural” spinors for the ground and low-lying excited states at \( R = R_e(\chi 1/2) \). One immediately notes that all these spinors are localized on the Ra atom and the shape of the corresponding density distributions is typical for non-bonding spinors or orbitals of Class I according to [4], except for the energetically lowest \( \Omega = 3/2 \) spinor, which is rather a Class II spinor. We would like to remind that Class I spinors are spinors which have most of their density out of the bonding region, due to e.g. destructive sp-hybridisation, and thus electrons occupying such spinors do not participate in chemical bonding. Class II spinors are “atomic-type” non-bonding spinors, which have a shape of atomic orbital centered on corresponding atom and cannot be shared between atoms (and thus create a chemical bond), due to symmetry reasons (see [4, 34] for details).

Calculations of \( P \)-odd and \( P, T \)-odd effects in the framework of a quasirelativistic ZORA approach attract considerable interest due to both importance of these effects for search for new physics (see [24] and [2]) and due to effective test of accuracy of quasirelativistic approaches in calculations of effects, heavily depending on relativity. In a number of papers [26, 27, 35] it was demonstrated that values from the ZORA approach deviate by less than 5% from values obtained with relativistic Dirac-Coulomb Hamiltonian for nuclear spin-dependent \( P \)-odd and scalar electron-nucleus \( P, T \)-odd interactions. Results of
Figure 2. Isodensity surfaces and cross sectional view for unpaired-electron pseudonatural spinor densities for low-lying electronic states of RaCl. Numbers in parenthesis enumerate spinors, whereas the adjacent number corresponds to the $\Omega$ value for each spinor.

our ZORA/GHF and ZORA/GKS calculations of nuclear spin-dependent $P$-odd and scalar electron-nucleus $P$, $T$-odd parameters are presented in Table V. In both ZORA/GHF and ZORA/GKS calculations, as it is expected and as found in previous numerical studies [36], chemical substitution in RaX compounds does not change considerably the magnitudes of $P$-odd and $P$, $T$-odd effects in molecules with non-bonding valence electron. Our results for RaCl confirm the common trend that accounting for electron correlation and spin-polarisation effects (see also [26] for discussion) lead to increase of nuclear spin-dependent $P$-odd effects in open-shell diatomic molecules with $\Sigma_{1/2}$ ground electronic states. It is interesting that with $P$, $T$-odd effects the situation is the opposite – it was previously observed that accounting for electron correlations decreases the absolute value of $W_s$ for about 10% in RaF (-152 kHz GHF vs. -136 kHz GKS/B3LYP in [37]). The same trend we observe in RaCl, absolute value for $W_s$ drops down to -154 kHz for GKS/B3LYP, which constitutes 7% decrease from the GHF result. We note that in contrast to our quasi-relativistic complex GHF approach to those fundamental symmetry violating effects, the paired generalised Dirac–Hartree–Fock (DHF) ansatz used in Ref. [36] does not capture spin-polarisation effects, so that coupled cluster with singles and doubles amplitude (CCSD) gives absolute
Table V. Results of ZORA/GHF and ZORA/GKS (with B3LYP exchange-correlation functional) calculations of $W_a$ and $W_s$ for the ground electronic $\Sigma_{1/2}$ state of RaCl.

|            | $W_a$, kHz | $W_s$, kHz |
|------------|------------|------------|
| RaCl RaF$^a$) RaOH$^b$) | 1.48       | 1.30       |
| ZORA/GHF   | 1.48       | 1.38       | -166       | -152       | -154       |
| ZORA/GKS   | 1.64       | 1.42       | -          | -154       | -136       |
| DHF        | -          | -          | -127.9$^d$ | -116.9$^d$ |
| CCSD       | -          | -          | -168.1$^d$ | -152.5$^d$ |

$^a$) data from [34] $^b$) data from [11] $^c$) data from [37] $^d$) data from [36]

values for the $\mathcal{P},\mathcal{T}$-odd parameters that are larger than their DHF counterparts.

IV. CONCLUSION

The electronic and vibronic structure of diatomic RaCl has been studied with relativistic Fock space coupled cluster methods. Based on the computed level energies, a reassignment of previously reported levels was proposed, suggesting that the states formerly assigned as $C, C'$ to a spin-orbit-split $^2\Pi$ level belong instead to the $(2)3/2$ level of $^2\Pi$ character and the $(3)1/2$ level of predominantly $^2\Sigma$ character. Computed potential energy surfaces for the energetically lowest electronic states are found to be nearly parallel to each other, suggesting a favourable situation for laser cooling. In agreement with the experimental report, a very narrow Franck–Condon parabola (nearly diagonal Franck–Condon matrix) is found and computed branching ratios strongly suggest amenability of RaCl for laser cooling.

As precursor materials for RaCl are more readily available than for RaF, this is excellent news for preparatory off-line studies on laser cooling and precision spectroscopy with radium monohalide molecules. Due to medical applications of $^{223}$RaCl$_2$ in radiotumor therapies, even shorter-lived isotopologues are commercially available, which offers opportunities to study nuclear spin-dependent properties and isotope effects with the title molecule.
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