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# Relativistic coupled-cluster calculations of RaOH pertinent to spectroscopic detection and laser cooling

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A relativistic coupled-cluster study of the low-lying electronic states in the radium monohydroxide molecule (RaOH), a radioactive polyatomic molecule of interest to laser cooling and to the search of new physics beyond the Standard Model, is reported. The level positions of the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states have been computed with an accuracy of around  $200\text{ cm}^{-1}$  to facilitate spectroscopic observation of RaOH using laser induced fluorescence spectroscopy, thereby exploiting the systematic convergence of electron-correlation and basis-set effects in relativistic coupled-cluster calculations. The energy level for the  $B^2\Delta_{3/2}$  state has also been calculated accurately to conclude that the  $B^2\Delta_{3/2}$  state lies above the  $A^2\Pi_{1/2}$  state. This confirms  $X^2\Sigma \leftrightarrow A^2\Pi_{1/2}$  as a promising optical cycling transition for laser cooling RaOH.

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## 1. Introduction

Recent years have seen a surge of interest in heavy-atom-containing radioactive molecules.<sup>1–4</sup> Small molecules containing radioactive elements, *e.g.*, Ra, Ac, or Pa offer sensitive and versatile avenues for precision spectroscopy search of fundamental physics beyond the Standard Model (BSM), including the search of the electron's electric dipole moment (eEDM), nuclear magnetic quadrupole moments (nMQM), and Schiff moments.<sup>5–21</sup> Furthermore, Ra(*i*) in many molecular species has the potential to serve as efficient optical cycling centers<sup>5,16,22–28</sup>; such radium-containing molecules are promising candidates for the application of laser-cooling and subsequent advanced quantum control techniques. High-resolution laser spectroscopy studies of the radium monofluoride (RaF) molecule have recently been reported,<sup>1,28–30</sup> and a laser-cooling scheme has been designed for RaF.<sup>28</sup> Optical mass spectroscopy detection of radium-containing molecular cations including  $\text{RaOH}^+$  and  $\text{RaOCH}_3^+$  has also been reported.<sup>31</sup>

Among the radium-containing molecular species, the neutral radium monohydroxide (RaOH) molecule is of significant interest. Computational studies have predicted an effective internal electric field of over  $50\text{ GV cm}^{-1}$  in the electronic ground state of RaOH; RaOH is a therefore a sensitive molecule to use in a search for the eEDM.<sup>5–7,14,17,22</sup> Since the <sup>225</sup>Ra

nucleus has an octupole deformation and low-lying nuclear excited states of opposite parity,<sup>32,33</sup> <sup>225</sup>RaOH might also have good sensitivity for a Schiff moment search. Compared with radium-containing diatomic species such as RaF, the degenerate vibrational first excited states of the bending modes in RaOH give rise to parity doublets that provide crucial robustness against systematics errors in precision measurements.<sup>34</sup> Precision measurement using laser-cooled triatomic molecules has recently been demonstrated using laser-cooled CaOH molecules loaded in an optical dipole trap (ODT).<sup>35</sup> Recent computational studies have also shown that the  $X^2\Sigma \leftrightarrow A^2\Pi_{1/2}$  transitions in RaOH can serve as efficient optical cycling transitions for laser slowing and cooling.<sup>36</sup> It seems to require fewer repumping lasers to slow a cryogenic RaOH molecular beam sufficiently to be loaded into a magneto-optical trap (MOT) than in the corresponding experiment for CaOH. Note that CaOH is currently the only triatomic molecule that has been laser-slowed in three dimension, loaded into a MOT,<sup>37</sup> sub-Doppler cooled, and loaded into an ODT<sup>38</sup> and optical tweezer arrays.<sup>39</sup> RaOH is a promising heavy-atom-containing triatomic molecule to realize the same level of advanced quantum control. The combination of laser spectroscopy, cooling, trapping, and advanced quantum state control and measurement of RaOH in principle offers a clear pathway to use RaOH in eEDM, nMQM, and Schiff moment measurement with enhanced sensitivity and versatility.

High-resolution laser spectroscopic detection and measurement of RaOH is a prerequisite for laser cooling of this molecule and the subsequent precision measurement. Laser spectroscopy studies of radioactive molecules are in general

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challenging, because of the need to deal with radioactivity, the relatively short window for observation, and the low concentration of the molecular sample. *Ab initio* quantum-chemical prediction of energies and properties plays an indispensable role in the spectroscopic measurement of radioactive molecules. For example, relativistic Fock-space coupled-cluster calculations of RaF have accurately predicted the level positions for electronic excited states of RaF that have greatly facilitated the recent experimental measurements of this molecule.<sup>1</sup> We focus this paper on relativistic coupled-cluster calculations of the low-lying electronic states of RaOH pertinent to its spectroscopic detection and laser cooling. Exploiting the ability of the exact two-component theory<sup>40–42</sup> for accounting for relativistic effects and that of the coupled-cluster theory<sup>43,44</sup> for treating electron-correlation effects, the present computational study aims to obtain accurate energy levels for the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states of RaOH to facilitate the spectroscopic detection of this molecule. Furthermore, the computational study also aims to answer an important question of relevance to laser cooling of RaOH: is the  $A^2\Pi_{1/2}$  state the lowest electronic excited state of RaOH? We present the computational methods in Section II. The results are discussed in Section III with a conclusion given in Section IV.

## II. Computational details

The calculations are focused on the electronic ground state,  $X^2\Sigma$ , and three low-lying electronic excited states,  $A^2\Pi_{1/2}$ ,  $B^2\Delta_{3/2}$ , and  $C^2\Sigma$ , in both RaF and RaOH. The open-shell spinors in the  $X^2\Sigma$ ,  $A^2\Pi_{1/2}$ , and  $B^2\Delta_{3/2}$  states are mainly composed of a radium 6s spinor, a radium 6p<sub>1/2</sub> spinor, and a radium 6d<sub>3/2</sub> spinor, respectively. The open-shell spinor in the  $C^2\Sigma$  state is a mixture of 50% a radium 6p<sub>3/2</sub> spinor and 50% a radium 6d<sub>3/2</sub> spinor. We have employed the Kramers unrestricted coupled-cluster singles and doubles (CCSD)<sup>45</sup> method and CCSD augmented with a non-iterative triples [CCSD(T)]<sup>46</sup> method to treat electron-correlation effects using Kramers unrestricted Hartree-Fock (HF) wave functions optimized specifically for each state as the reference functions. The HF wave functions for the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states have been obtained by specifying occupation numbers based on the dominating orbital angular momenta of the HF spinors. We have also carried out calculations with the electron attachment version of equation-of-motion coupled-cluster singles and doubles (EOMEA-CCSD)<sup>47–49</sup> method for comparison using the closed-shell cation as the reference function. Since radium is a heavy atom, it is necessary to treat relativistic effects rigorously to obtain accurate results. We have used the exact two-component theory with atomic mean-field integrals based on the Dirac-Coulomb-Breit Hamiltonian (the X2CAMF scheme)<sup>50,51</sup> to treat relativistic effects in our calculations. All these calculations have been carried out using the CFOUR program.<sup>52–55</sup> In addition, to study high-level correlation (HLC) contributions, namely, electron-correlation contributions beyond CCSD(T), we have carried out CC singles doubles triples (CCSDT)<sup>56,57</sup> and CCSDT augmented with a non-iterative quadruples [CCSDT(Q)]<sup>58</sup> calculations. These CCSDT and CCSDT(Q) calculations have used the

MRCC program<sup>59–61</sup> with an interface with the CFOUR program, using the implementation of the spin-free exact two-component theory in its one-electron variant (the SFX2C-1e scheme) in the CFOUR program<sup>62,63</sup> to treat scalar-relativistic effects. These calculations have been performed for the term energies of the  $A^2\Pi$  and  $B^2\Delta$  states. We have not performed SFX2C-1e calculations for the  $C^2\Sigma$  state, since the specification of the HF occupation numbers based on orbital angular momenta has not been implemented in the CFOUR program for the calculations without spin-orbit coupling. We have performed calculations for RaOH and RaF using the same computational protocol. The computational results for RaF are then compared with available measured and computed values<sup>1,29,30</sup> to help assess the accuracy of the calculations for RaOH. The present calculations aim at an accuracy of 100–200 cm<sup>−1</sup> for the term energies of the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states to facilitate using these two states in spectroscopic detection of RaOH. The present study also aims to calculate the term energy of the  $B^2\Delta_{3/2}$  state with sufficient accuracy to determine its relative position with respect to the  $A^2\Pi_{1/2}$  state. We base our calculations on the generic idea of theoretical model chemistries (also referred to as additivity schemes or composite schemes),<sup>64–70</sup> which have been extensively studied in calculations of atomization energies for molecules aiming at chemical or subchemical accuracies. The chemical accuracy and subchemical accuracy correspond to 1 kcal mol<sup>−1</sup> (around 300 cm<sup>−1</sup>) and 1 kJ mol<sup>−1</sup> (around 80 cm<sup>−1</sup>), respectively. The term energies targeted in the present study are energy differences between different electronic states of a same molecule. These calculations in general have more favorable error cancellation than calculations of atomization energies, which involve breaking of chemical bonds. An accuracy of 100–200 cm<sup>−1</sup> is feasible with the available computational resources.

Following the idea of an additivity scheme, we perform geometry optimizations at the X2CAMF-CCSD(T) level of theory that provide sufficiently accurate molecular structures, and then carry out X2CAMF-CCSD(T) calculations of electronic energies with systematically enlarged basis sets using these structures. Specifically, the equilibrium structures of the  $X^2\Sigma$ ,  $A^2\Pi_{1/2}$ ,  $B^2\Delta_{3/2}$ , and  $C^2\Sigma$  states of RaOH and RaF have been computed at the X2CAMF-CCSD(T) level using the uncontracted ANO-RCC basis set for Ra<sup>71,72</sup> and the uncontracted cc-pVTZ basis sets for O, H, and F.<sup>73</sup> The Ra 5s, 5p, 5d, 6s electrons, the 2s and 2p electrons of O and F, and the 1s electrons of H have been correlated in these calculations. Based on benchmark studies of CCSD(T) accuracy for molecular structures,<sup>74</sup> the present calculations aim at an accuracy of 0.01 Å for the bond lengths. X2CAMF-EOMEA-CCSD calculations have also been carried out for comparison. The harmonic vibrational frequencies have been calculated to obtain the zero-point vibrational energies within the harmonic approximation. The equilibrium structures and harmonic vibrational frequencies for RaF have been obtained by fitting local potential energy surfaces around the equilibrium bond lengths. The calculations of equilibrium structures for RaOH have been facilitated by the recent development of analytic X2CAMF-CCSD(T) and EOM-CCSD gradients.<sup>75</sup> The harmonic vibrational frequencies of RaOH have been evaluated by means of numerical differentiation of analytically evaluated gradients.<sup>76</sup>

The electronic energies for the  $X^2\Sigma$ ,  $A^2\Pi_{1/2}$ ,  $B^2\Delta_{3/2}$ , and  $C^2\Sigma$  states of RaF and RaOH have been calculated at the HF, CCSD, and CCSD(T) levels with systematically enlarged basis sets using the X2CAMF-CCSD(T) equilibrium structures. It is essential to saturate the treatment of basis-set effects to obtain accurate electronic energies. We have systematically extended the uncontracted ANO-RCC basis set of Ra to form uncontracted basis sets of triple-, quadruple-, and quintuple-zeta quality, denoted as the ANOTZ, ANOQZ, and ANO5Z sets, respectively. Specifically, the primitive set of s-, p-, d-, and f-type functions in the ANO-RCC set (28s25p17d13f) is augmented with two additional diffuse d-type functions with exponents 0.0130943 and 0.0043648, as well as one diffuse f-type functions with an exponent 0.0135, to form the ANOTZ (28s25p19d14f) set. The exponents of these additional functions are obtained by multiplying those of the most diffuse functions in the ANO-RCC set with a geometric factor of 1/3. The ANOQZ set is obtained by augmenting the ANOTZ set with four g-type functions with exponents 0.9705, 0.3235, 0.1075, and 0.043. The ANO5Z set is constructed by augmenting the ANOTZ set with six g-type functions with exponents 9.1368, 3.0456, 1.0152, 0.3384, 0.0919, and 0.0368, and four h-type functions with exponents 1.1268, 0.3756, 0.1114, 0.0446. These exponents been obtained to cover the exponent range of the g- and h-type functions in the Ra aug-cc-pCV5Z-PP set.<sup>77</sup> The combined sets of ANOXZ (X = T, Q, 5) with the corresponding uncontracted aug-cc-pVXZ sets of O, H, and F are denoted as the XZ (X = T, Q, 5) sets.<sup>73</sup> The X2CAMF-HF/5Z energies are used to estimate the basis-set-limit values of the HF energies. The X2CAMF-CCSD and CCSD(T) correlation energies obtained using the QZ and 5Z sets are extrapolated using a simple two-point formula<sup>78</sup>

$$E_{\text{corr}}(\infty Z) = E_{\text{corr}}(XZ) - \frac{c}{X^3}, \quad (1)$$

to estimate the basis-set-limit values for correlation energies. These calculations have been carried out with the correlation of

27 valence and semicore electrons, namely, the Ra 5s, 5p, 5d, 6s electrons, the 2s and 2p electrons of O and F, and 1s electrons of H. Finally, the contributions from correlating inner-shell electrons are obtained as the differences between the X2CAMF-CCSD(T)/TZ energies with the correlation of 69 electrons (freezing only the Ra 1s, 2s, 2p, 3s, 3p, and 3d electrons) and those with the correlation of 27 electrons. For the calculation of HLC contributions, correlation-consistent triple-zeta basis sets contracted for the SFX2C-1e scheme<sup>77</sup> have been used with the correlation of the Ra 5s, 5p, 5s electrons, the O and F 2s and 2p electrons, and the H 1s electrons. A Gaussian-type nuclear model<sup>79</sup> has been used for the calculations presented here.

### III. Results and discussions

#### A. The equilibrium structures and harmonic vibrational frequencies

The equilibrium structures and harmonic vibrational frequencies of the  $X^2\Sigma$ ,  $A^2\Pi_{1/2}$ ,  $B^2\Delta_{3/2}$ , and  $C^2\Sigma$  states of RaOH computed at X2CAMF-CCSD(T) and EOMEA-CCSD levels are summarized in Table 1. Since the electronic excitations are localized at the radium atom, these four electronic states share similar structures. The Ra–O bond lengths of these states differ from each other by less than 0.01 Å, while the differences in the O–H bond lengths are smaller than 0.001 Å. The X2CAMF-EOMEA-CCSD structures are consistent with the X2CAMF-CCSD(T) ones, with discrepancies less than 0.01 Å for the bond lengths presented here. The X2CAMF-EOMEA-CCSD harmonic frequencies also agree well with the X2CAMF-CCSD(T) ones for the  $X^2\Sigma$  and  $A^2\Pi_{1/2}$  states. Because of the difficulty to converge the corresponding Kramers unrestricted Hartree–Fock wave functions in the displaced bent structures, we have not obtained X2CAMF-CCSD(T) harmonic frequencies for the  $B^2\Delta_{3/2}$  and  $C^2\Sigma$  states. We have included X2CAMF-EOMEA-CCSD harmonic vibrational frequencies for these two states.

**Table 1** Computed structural parameters, harmonic vibrational frequencies, and equilibrium term energies for the electronic ground and low-lying excited states of RaOH and RaF. The uncontracted ANO-RCC basis set for Ra and the uncontracted cc-pVTZ basis sets for O, H, and F have been used for all calculations

		$X^2\Sigma$	$A^2\Pi_{1/2}$	$B^2\Delta_{3/2}$	$C^2\Sigma$
RaOH <sup>a</sup>	$R_e$ (Ra–O) (Å)	2.265 (2.269)	2.260 (2.264)	2.268 (2.276)	2.268 (2.272)
	$R_e$ (O–H) (Å)	0.956 (0.953)	0.956 (0.952)	0.956 (0.952)	0.956 (0.952)
	$\omega_e$ [Ra–O stretch] ( $\text{cm}^{-1}$ )	490 (488)	495 (492)	— <sup>b</sup> (495)	— <sup>b</sup> (487)
	$\omega_e$ [Ra–O–H bend] ( $\text{cm}^{-1}$ )	354 (363)	387 (395)	— <sup>b</sup> (345)	— <sup>b</sup> (435)
	$\omega_e$ [O–H stretch] ( $\text{cm}^{-1}$ )	3912 (3969)	3919 (3973)	— <sup>b</sup> (3977)	— <sup>b</sup> (3970)
	$T_e$ ( $\text{cm}^{-1}$ )	0 (0)	12924 (12 929)	15 247 (15 257)	15 955 (16 019)
RaF <sup>a</sup>	$R_e$ (Ra–F) (Å)	2.251 (2.253)	2.254 (2.256)	2.266 (2.268)	2.271 (2.273)
	$\omega_e$ [Ra–F stretch] ( $\text{cm}^{-1}$ )	438 (437)	434 (433)	424 (423)	425 (423)
	$T_e$ ( $\text{cm}^{-1}$ )	0 (0)	13 499 (13 502)	14 935 (14 936)	16 884 (16 944)
RaF <sup>c</sup>	$R_e$ (Ra–F) (Å)	2.244	2.247	2.258	2.262
	$\omega_e$ [Ra–F stretch] ( $\text{cm}^{-1}$ )	441	437	431	432
	$T_e$ ( $\text{cm}^{-1}$ )	0 (0)	13 303	14 352	16 644
RaF <sup>d</sup>	$\omega_e$ [Ra–F stretch] ( $\text{cm}^{-1}$ )	442	436	—	—
	$T_e$ ( $\text{cm}^{-1}$ )	0 (0)	13 288	—	16 621

<sup>a</sup> X2CAMF-CCSD(T) values with EOMEA-CCSD results in the parentheses. <sup>b</sup> Not calculated due to difficulty in HF convergence for displaced structures. <sup>c</sup> Computed values in ref. 29. <sup>d</sup> Measured values in ref. 1.

Interestingly, while the four electronic states studied here have similar Ra–O and O–H stretching frequencies, the bending frequencies show relatively large variations. The bending frequency of  $435\text{ cm}^{-1}$  for the  $\text{C}^2\Sigma$  state is around  $70\text{ cm}^{-1}$  greater than that of the  $\text{X}^2\Sigma$  state.

We have also included X2CAMF-CCSD(T) and EOMEA-CCSD results for RaF in Table 1 and compared them with available computed and measured values.<sup>1,29</sup> Similar to the case of RaOH, these four electronic states of RaF have similar bond lengths. The difference between the Ra–F bond lengths in the  $\text{C}^2\Sigma$  state and the  $\text{X}^2\Sigma$  state amounts to around  $0.02\text{ \AA}$ , slightly larger than that in RaOH. The X2CAMF-EOMEA-CCSD bond lengths and harmonic frequencies are consistent with the X2CAMF-CCSD(T) values. The present computational results for RaF agree reasonably well with available computed and measured results. The X2CAMF-CCSD(T) Ra–F bond lengths are around  $0.007\text{--}0.009\text{ \AA}$  longer than the four-component CC results in ref. 29. We expect further enlargement of basis sets in X2CAMF-CCSD(T) calculations to slightly reduce the Ra–F bond lengths. The X2CAMF-CCSD(T) harmonic frequencies for the  $\text{B}^2\Delta_{3/2}$  and  $\text{C}^2\Sigma$  states are slightly smaller than the computed values in ref. 29, by around  $7\text{ cm}^{-1}$ .

## B. Electronic energies

The equilibrium term energies obtained in the structural optimizations are also listed in Table 1. The results for the  $\text{A}^2\Pi_{1/2}$  and  $\text{C}^2\Sigma$  states of RaF agree reasonably well with the measured values and lie around  $200\text{--}300\text{ cm}^{-1}$  above the measured values. The equilibrium term energy for the  $\text{B}^2\Delta_{3/2}$  state exhibits a relatively large discrepancy, lying around  $600\text{ cm}^{-1}$  above the computed value in ref. 29. The corresponding equilibrium term energies for RaOH in Table 1 are expected to have similar accuracies. The discrepancies for RaF observed here can be attributed to basis-set effects. In particular, the  $\text{B}^2\Delta_{3/2}$  state has the unpaired electron occupying a radium 6d orbital. Since the differential angular momentum with respect to the ground state is large, the term energy of the  $\text{B}^2\Delta_{3/2}$  state is sensitive to basis-set effects. It thus is necessary to treat basis-set effects more thoroughly to improve the accuracy of the results.

Basis-set convergence of the HF, CCSD, and (T) contributions to the equilibrium term energies are summarized in Table 2. As expected, the HF energies converge rapidly with respect to the enlargement of basis sets. The HF/5Z term energies differ from the HF/QZ results by less than  $3\text{ cm}^{-1}$ . The electron-correlation contributions including the CCSD and (T) contributions exhibit larger basis-set effects. Since the excited states have the unpaired electrons in p- or d-type spinors with angular momenta higher than that in the ground state, the basis-set effects in general reduce the term energies. The TZ CCSD contributions to the term energies of the  $\text{A}^2\Pi_{1/2}$  and  $\text{C}^2\Sigma$  states amounts to  $1448\text{ cm}^{-1}$  and  $1689\text{ cm}^{-1}$ , respectively. They are  $148\text{ cm}^{-1}$  and  $118\text{ cm}^{-1}$  greater than the corresponding  $\infty\text{Z}$  values of  $1300\text{ cm}^{-1}$  and  $1571\text{ cm}^{-1}$ . The basis-set effects on the energies of the  $\text{B}^2\Delta_{3/2}$  state having the unpaired electron in a radium 6d spinor is substantially more significant. The TZ electron-correlation contribution to

**Table 2** Equilibrium term energies ( $\text{cm}^{-1}$ ) for the low-lying excited states of RaOH. The X2CAMF scheme has been used to account for relativistic effects

		$\text{A}^2\Pi_{1/2}$	$\text{B}^2\Delta_{3/2}$	$\text{C}^2\Sigma$
HF-SCF	TZ	11 280	14 925	13 873
	QZ	11 273	14 913	13 874
	5Z	11 270	14 916	13 875
CCSD	TZ	1448	248	1689
	QZ	1368	−241	1626
	5Z	1335	−397	1599
	$\infty\text{Z}$	1300	−559	1571
(T)	TZ	138	62	153
	QZ	151	12	172
	5Z	158	−15	181
	$\infty\text{Z}$	166	−44	191
Core correlation	TZ	22	56	37
Total		12 758	14 368	15 673

the term energy of the  $\text{B}^2\Delta_{3/2}$  state, namely, the sum of CCSD and (T) contributions, amount to  $278\text{ cm}^{-1}$ . This is to be compared with the basis-set-limit value of  $−611\text{ cm}^{-1}$ ; the remaining basis-set effects for the TZ result is as large as around  $900\text{ cm}^{-1}$ . The correlation of inner-shell electrons make minor contributions to these equilibrium term energies, amounting to  $22\text{ cm}^{-1}$ ,  $56\text{ cm}^{-1}$ , and  $37\text{ cm}^{-1}$  for the  $\text{A}^2\Pi_{1/2}$ ,  $\text{B}^2\Delta_{3/2}$ , and  $\text{C}^2\Sigma$  states, respectively.

A corresponding study of basis-set effects on the equilibrium term energies of the  $\text{A}^2\Pi_{1/2}$ ,  $\text{B}^2\Delta_{3/2}$ , and  $\text{C}^2\Sigma$  states in RaF are summarized in Table 3. Electron-correlation contributions and convergence patterns similar to those of RaOH have been observed. This similarity might indicate that the quality of the present computational results for RaOH is similar to that for RaF.

## C. Assessment of the computational accuracy

The remaining errors for the computed equilibrium term energies include the errors due to the molecular structures, the errors in the estimate of the basis-set-limit values, the high-level correlation contributions beyond CCSD(T), and the quantum electrodynamics (QED) corrections. In this subsection we analyze these contributions and estimate the magnitude of the remaining errors for the computed equilibrium term energies.

The accuracy of the computed bond lengths is around  $0.01\text{ \AA}$ . We have carried out calculations by varying the bond lengths and found that a variation of  $0.02\text{ \AA}$  for the Ra–O or Ra–F bond length correspond to a variation of around  $15\text{ cm}^{-1}$  for the computed term energies. It thus is safe to conclude that the remaining errors for the term energies due to the errors in the molecular structures are smaller than  $20\text{ cm}^{-1}$ . We should mention that an accuracy of  $0.01\text{ \AA}$  in bond length is not sufficient to guarantee an accuracy of  $80\text{ cm}^{-1}$  for the calculation of bond energies, e.g., an O–H bond energy. It has been shown that an accuracy of  $0.005\text{ \AA}$  for the bond lengths is required to achieve subchemical accuracy.<sup>66</sup> On the other hand, in the present calculations, all the electronic states have



**Table 3** Equilibrium term energies ( $\text{cm}^{-1}$ ) for the low-lying excited states of RaF. The X2CAMF scheme has been used to account for relativistic effects

		$A^2\Pi_{1/2}$	$B^2\Delta_{3/2}$	$C^2\Sigma$
HF-SCF	TZ	11 859	14 855	14 693
	QZ	11 859	14 848	14 712
	5Z	11 860	14 852	14 716
CCSD	TZ	1447	206	1817
	QZ	1351	−195	1736
	5Z	1311	−390	1705
	$\infty Z$	1268	−594	1672
(T)	TZ	140	72	173
	QZ	152	−1	194
	5Z	161	−9	205
	$\infty Z$	170	−17	216
Core correlation	TZ	26	64	40
Total		13 324	14 305	16 643

essentially the same O–H bond lengths; the errors in the O–H bond energies do not contribute significantly to the targeted term energies.

As shown in Tables 2 and 3, the basis-set convergence for both HF and electron-correlation energies has been observed to be smooth. Since the 5Z term energies of the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states differ from the basis-set-limit values estimated through basis-set extrapolation by around  $30 \text{ cm}^{-1}$ , we expect that the errors in the estimated basis-set-limit values are smaller than  $20 \text{ cm}^{-1}$ . The (T) contributions to the term energies of the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states are  $166 \text{ cm}^{-1}$  and  $191 \text{ cm}^{-1}$ , respectively. Both of them are an order of magnitude smaller than the corresponding CCSD contributions. The high-level correlation (HLC) contributions, those beyond CCSD(T), thus are expected to further decrease significantly compared with the (T) contributions. It seems logical to assume that they are smaller than  $60 \text{ cm}^{-1}$ . We have computed the HLC contributions to the term energy of the  $A^2\Pi$  state as the difference between SFX2C-1e-CCSDT(Q), CCSDT, and CCSD(T) calculations using correlation-consistent triple-zeta basis sets. The full triples correction, namely, the difference between CCSDT and CCSD(T), amounts to around  $2 \text{ cm}^{-1}$ . The quadruples contribution obtained as the difference between the CCSDT(Q) and CCSDT results is around  $4 \text{ cm}^{-1}$ . While they used smaller basis sets and correlation space without including spin-orbit coupling, these calculations serve as a confirmation that  $60 \text{ cm}^{-1}$  is a conservative estimate for the HLC contributions. While we have included the contribution

from the Breit term in the X2CAMF scheme, we have not included the QED corrections. The QED contributions to the term energies of the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states in RaF have been estimated to be around  $-50 \text{ cm}^{-1}$ .<sup>29</sup> An uncertainty of  $50 \text{ cm}^{-1}$  will be used here for RaOH as well.

If we assume that these four remaining uncertainties are statistically independent of each other, the remaining errors for the computed equilibrium term energies of the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states is estimated to be around  $80 \text{ cm}^{-1}$ . To be conservative about the error estimate, we use twice this estimate, namely  $160 \text{ cm}^{-1}$ , as the estimate of the errors for these computed term energies. The final results for the equilibrium term energies of the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states in RaOH thus are  $12758 \pm 160 \text{ cm}^{-1}$  and  $15673 \pm 160 \text{ cm}^{-1}$ , respectively. We should mention that the computed term energies for the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states of RaF are only around  $40 \text{ cm}^{-1}$  and  $20 \text{ cm}^{-1}$  larger than the measured values, as shown in Table 4. Since the electron-correlation contributions in RaOH take similar values and show similar convergence patterns as those in RaF, the present computational results for RaOH might have similar accuracies. Therefore, this estimated error of  $160 \text{ cm}^{-1}$  serves as a conservative estimate of the errors. Since the present study is focused on one molecule, the error estimate does not rigorously correspond to 95% confidence intervals defined in a statistical sense.<sup>80</sup> On the other hand, the conservative estimate of the errors indicates that the actual error is unlikely larger than the estimate. This error of  $160 \text{ cm}^{-1}$  thus may be viewed as an estimate of 95% confidence intervals in practice.

The contributions from the zero-point vibrational energies (ZPE) to the term energies of  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states in RaOH amount to  $36 \text{ cm}^{-1}$  and  $68 \text{ cm}^{-1}$ , respectively, using the harmonic vibrational frequencies in Table 1. These agree well with the corresponding corrections of  $40 \text{ cm}^{-1}$  and  $76 \text{ cm}^{-1}$  obtained in our previous multi-state vibronic calculations.<sup>36</sup> We adopt the latter values, since they include the anharmonic contributions. Adding these ZPE contributions to the equilibrium term energies, we recommend the values of  $12798 \pm 160 \text{ cm}^{-1}$  and  $15749 \pm 160 \text{ cm}^{-1}$  as the level positions for the vibrational origin transitions for the  $A^2\Pi_{1/2}$ - $X^2\Sigma$  and  $C^2\Sigma$ - $X^2\Sigma$  electronic transitions, respectively, for spectroscopic detection of RaOH using laser induced fluorescence spectroscopy. In the case of RaOD, the ZPE corrections to the term energies of  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states amount to  $31 \text{ cm}^{-1}$  and  $57 \text{ cm}^{-1}$  in the multi-state vibronic calculations. The level positions for the vibrational origin transitions for the  $A^2\Pi_{1/2}$ - $X^2\Sigma$  and  $C^2\Sigma$ - $X^2\Sigma$  electronic transitions in RaOD thus are predicted to take the

**Table 4** Computed equilibrium term energies ( $\text{cm}^{-1}$ ) for the low-lying excited states of RaOH together with the corresponding values for RaF computed using the same computational protocol and compared with results in the literature

		$A^2\Pi_{1/2}$	$B^2\Delta_{3/2}$	$C^2\Sigma$
RaOH	This work	12 758	14 368	15 673
RaF	This work	13 324	14 305	16 643
	Computed values in ref. 29	13 303	14 352	16 644
	Computed values in ref. 30	13 299(36)	14 300(61)	16 615(69)
	Measured values in ref. 1	13 284.7(5)	—	16 620.8(2)
	Measured values in ref. 30	13 284.427(1)	14 332.82(13)	16 613.6(12)

values of  $12789 \pm 160 \text{ cm}^{-1}$  and  $15730 \pm 160 \text{ cm}^{-1}$ , respectively.

The computed equilibrium term energy for the  $B^2\Delta_{3/2}$  state of RaOH is around  $1600 \text{ cm}^{-1}$  greater than the  $A^2\Pi_{1/2}$  state. The HLC contribution for the term energy of the  $B^2\Delta_{3/2}$  state obtained in the present calculations is around  $-3 \text{ cm}^{-1}$ . This confirms that the estimated error of  $60 \text{ cm}^{-1}$  in the treatment of electron correlation is also conservative for the  $B^2\Delta_{3/2}$  state. Since the equilibrium term energy of the  $B^2\Delta_{3/2}$  state is more sensitive to the basis-set effects, the overall estimated uncertainty is slightly larger than those of the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states but is still smaller than  $200 \text{ cm}^{-1}$ . The present computational study thus has definitely placed the  $B^2\Delta_{3/2}$  state above the  $A^2\Pi_{1/2}$  state and predicted the  $A^2\Pi_{1/2}$  state to be the lowest electronic excited state of RaOH. The  $X^2\Sigma \leftrightarrow A^2\Pi_{1/2}$  electronic transition hence does not have any intermediate electronic state and can serve as efficient optical cycling transition for laser cooling of RaOH.

## IV. Conclusion

We report a relativistic coupled-cluster study of low-lying electronic states of RaOH, a radioactive triatomic molecule of significant interest to laser cooling and search of new physics. The calculated term energies of  $12798 \pm 160 \text{ cm}^{-1}$  and  $15749 \pm 160 \text{ cm}^{-1}$  for the  $A^2\Pi_{1/2}$  and  $C^2\Sigma$  states and the computed vibrational frequencies presented here will expedite the observation and identification of RaOH, which can be produced with on-line methods at radioactive beam facilities<sup>1,81,82</sup> as well as table-top methods using cryogenic buffer gas cooling.<sup>83</sup> The calculations also predict the  $B^2\Delta_{3/2}$  state to lie substantially above the  $A^2\Pi_{1/2}$  state; the  $A^2\Pi_{1/2}$  state is the lowest electronic excited state in RaOH. Laser slowing of RaOH using optical cycling of the  $X^2\Sigma \leftrightarrow A^2\Pi_{1/2}$  transitions, which have favorable vibronic branching ratios, thus is highly recommended.

## Conflicts of interest

The authors report there are no competing interests to declare.

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