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# On the Feasibility of Rovibrational Laser Cooling of Radioactive $\text{RaF}^+$ and $\text{RaH}^+$ Cations

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**Abstract:** Polar radioactive molecules have been suggested to be exceptionally sensitive systems in the search for signatures of symmetry-violating effects in their structure. Radium monofluoride ( $\text{RaF}$ ) possesses an especially attractive electronic structure for such searches, as the diagonality of its Franck-Condon matrix enables the implementation of direct laser cooling for precision experiments. To maximize the sensitivity of experiments with short-lived  $\text{RaF}$  isotopologues, the molecular beam needs to be cooled to the rovibrational ground state. Due to the high kinetic energies and internal temperature of extracted beams at radioactive ion beam (RIB) facilities, in-flight rovibrational cooling would be restricted by a limited interaction timescale. Instead, cooling techniques implemented on ions trapped within a radiofrequency quadrupole cooler-buncher can be highly efficient due to the much longer interaction times (up to seconds). In this work, the feasibility of rovibrationally cooling trapped  $\text{RaF}^+$  and  $\text{RaH}^+$  cations with repeated laser excitation is investigated. Due to the highly diagonal nature between the ionic ground state and states in the neutral system, any reduction of the internal temperature of the molecular ions would largely persist through charge-exchange without requiring the use of cryogenic buffer gas cooling. Quasirelativistic X2C and scalar-relativistic ECP calculations were performed to calculate the transition energies to excited electronic states and to study the nature of chemical bonding for both  $\text{RaF}^+$  and  $\text{RaH}^+$ . The results indicate that optical manipulation of the rovibrational distribution of trapped  $\text{RaF}^+$  and  $\text{RaH}^+$  is unfeasible due to the high electronic transition energies, which lie beyond the capabilities of modern laser technology. However, more detailed calculations of the structure of  $\text{RaH}^+$  might reveal possible laser-cooling pathways.

**Keywords:** molecular electronic structure; radioactive molecules; molecular spectroscopy

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## 1. Introduction

In recent decades, the high-precision spectroscopy of atomic and molecular beams within reverting electromagnetic fields has emerged as a highly sensitive technique to search for physics beyond the Standard Model, potentially probing energy scales a few orders of magnitude greater than the capabilities of state-of-the-art particle colliders [1].

The structure of the diatomic  $\text{RaF}$  molecule has been proposed as especially attractive for tabletop experiments that probe the extent of fundamental symmetry violations in the universe [2,3], owing to its enhanced sensitivity to symmetry-violating effects within the radium nucleus [4,5] and the highly diagonal Franck-Condon matrix for vibronic transitions between the ground and low-lying excited electronic states that allow for direct laser cooling [6].

Recently, a milestone in the study of compounds of short-lived nuclei was achieved, with the first laser-spectroscopic study of RaF molecules containing different isotopes of Ra [6]. The technique of Isotope Separation On-Line (ISOL) at the ISOLDE radioactive ion beam (RIB) facility at CERN was combined with Collinear Resonance Ionization Spectroscopy (CRIS) [7] to measure the vibronic spectra of short-lived  $^{223-226,228}\text{RaF}$  molecules. The successful laser-spectroscopic campaign on isotopically pure molecular beams of RaF at the CRIS experiment paves the way for designing experiments to measure the extent of symmetry-violating effects in their spectra and other systems which can be produced at RIB facilities.

To maximize the precision of such experiments, the most developed of which are searching for small variations in the coherent precession of electrons within the internal molecular fields, the molecular beam should exist entirely in a single rovibrational state. In this case, the experimental count rate is maximized without needing to compromise the spectroscopic resolution.

However, through the ISOL technique, the radioactive molecules are extracted from solid targets as ionic species, which at the later stage have to be neutralised, at temperatures typically above 2000 °C, and accelerated to kinetic energies of 30–60 keV upon extraction [8]. The elevated target temperature is required to enhance the diffusion of short-lived species of interest from the interior of the target, while the high kinetic energy is a prerequisite for the efficient operation of the isotopic separation of the ionized beam. As a result, experiments aiming to perform high-precision searches for symmetry-violating effects in the extracted molecular beams need to compensate for the translational and rovibrational energy of the molecules in a reliable and efficient manner.

One of the important features of RaF ( $\text{RaF}^+$ ) molecules is the quasideagonality of the Franck-Condon matrix for neutralisation transitions  $^0\Sigma \rightarrow ^2\Sigma$  between the electronic ground state of the  $\text{RaF}^+$  cation and the electronic ground state of neutral RaF. Thus, given the highly diagonal nature of transitions between the ionic ground state and low-lying states in the neutral system, any reduction in the vibrational temperature of the  $\text{RaF}^+$  can be expected to persist through charge-exchange, yielding an improved spectroscopic sensitivity.

In this work, the electronic structure of the ground and lowest-lying excited electronic states of the  $\text{RaF}^+$  cation is investigated to assess the prospect of rovibrational cooling through spectrally shaped femtosecond optical pumping with commercially available laser systems. The electronic transition energies of  $\text{RaF}^+$  are also compared to those of the  $\text{RaH}^+$  cation.

## 2. Current Prospects for Experiments on RaF

In addition to searches for  $P,T$ -violating effects, the systematic study of isotopologue shifts in the transition frequencies of RaF has demonstrated that the molecular electronic structure can be exceptionally sensitive to differences in the nuclear size between isotopes [9]. Therefore, particularly for unstable isotopes that either cannot be extracted from the ISOL target in atomic form, or whose study is significantly hindered by isobaric contamination, a possible experimental pathway for extending the current limits of laser spectroscopy for nuclear structure may utilize molecular beams to study nuclear size effects.

However, for the study of isotopes far from nuclear stability, which may be produced at rates significantly below  $10^3$  nuclei per second, the percentage of molecules that are initially at a common lower rovibronic state becomes the main limitation for performing laser spectroscopy to extract nuclear structure observables. The CRIS experiment at ISOLDE has successfully studied atomic species with production yields as low as 20 nuclei per second in the past [10]. Even at room temperature however, which the molecules can reach after being trapped for a few milliseconds in a buffer-gas-cooled ion trap, the vibrational state distribution of RaF would result in less than 70% of the molecular ion beam in the vibronic ground state. Within this, the molecules are further distributed across numerous rotational states. As a result, without additional rovibrational cooling, the

capability of performing high-resolution molecular spectroscopy of RaF at RIB facilities would be reached for isotopologues with production yields considerably higher than the limit for atomic systems.

Rovibrationally cooling the molecular beam results in the compression of the energy state distribution of the molecules to only the lowest levels, increasing the population fraction that shares a common lower state during laser excitation. At RIB facilities, the implementation of rovibrational cooling of molecular beams faces additional challenges compared to non-radioactive laboratories. Firstly, efficient rovibrational cooling of radioactive molecules can require timescales that can be comparable to the radioactive half-life of the beam. In typical collinear laser spectroscopy experiments at RIB facilities, isotopes with half-lives as low as a few milliseconds can be studied [11]. Secondly, the beam properties and high kinetic energy of the ion beam must be preserved to ensure the efficient transmission and separation of radioactive molecules with low production yields.

While in-flight rovibrational cooling techniques would have very limited interaction times at these kinetic energies (typically 30–60 keV), such facilities often also incorporate a radiofrequency quadrupole trap that provides cooling and bunching of the radioactive beams using a room-temperature, inert buffer gas and quadrupole oscillating fields [12–14], with the possibility of laser access in the trap [15]. As the cooling and bunching of the ion beams of interest takes place on timescales of up to seconds, conditioning the molecular beams within the RFQ trap could provide a pathway for rovibrational cooling.

Rovibrational cooling via collisions with a cryogenic buffer gas [16] and via optical pumping with a spectrally shaped femtosecond laser [17] are techniques compatible with the requirements of RIB facilities and which can take advantage of the cooler-buncher in a straight-forward manner. Rovibrational cooling in a cryogenic buffer-gas cell is a state-of-the-art technique with widespread usage in molecular spectroscopy, in which a slow molecular beam flies through a cell filled with cryogenic helium or neon, or the beam is directly created within the cell, most often through laser ablation. In-flight cooling in a gas cell, however, is incompatible with the typical kinetic energies of delivered radioactive beams at RIB facilities. Instead, efficient cryogenic buffer-gas cooling must be done within a cryogenic cooler-buncher, in lieu of the typically room-temperature cooler-bunchers currently in use at the various RIB facilities, or by adding a deceleration region and a cryogenic buffer gas cell following the room-temperature RFQ.

An alternative route to reducing the internal energy of molecules produced at RIB facilities relies on directly manipulating the vibrational population using laser light. This technique was first experimentally realized on photo-associated  $\text{Cs}_2$  molecules [18]. Assembly of molecules from ultracold atoms often leaves the resulting molecules in a number of vibrational states of the electronic ground state, despite the ensemble being translationally cold. In this approach, a broadband laser is used to selectively excite an electronic transition that, after a number of excitation-deexcitation cycles, optically pumps a large fraction of the population to the vibrational ground state. This is achieved by spectrally shaping the frequency output of the laser to exclude the wavelengths that would lead to excitations from the vibrational ground state, which therefore acts as a dark state where all the molecules eventually accumulate. The technique was later extended to allow efficient transfer of  $\text{Cs}_2$  molecules to an arbitrary vibrational state of the electronic ground state [19]. Due to its relative simplicity, the technique has been applied to different systems (a review of which can be found in [20]). Once the molecules have been transferred to the vibrational ground state, the internal temperature can be further reduced by selectively exciting P-branch rotational transitions using similar spectral filtering techniques [21].

Realizing these techniques requires a tunable broadband laser, often a femtosecond titanium-sapphire system, with a frequency output that is sufficiently wide to encompass the necessary components of the molecular structure (typically tens of  $\text{cm}^{-1}$ ). The spectral density of such systems is inevitably poor and therefore requires long interaction times (milliseconds to seconds) to achieve a significant population transfer. The majority of these studies have therefore taken place in a trap. However, one study was able to significantly

rovibrationally cool a supersonic beam of BaF in less than 500  $\mu\text{s}$ , owing to the development of custom laser systems that deliver a higher spectral density in the wavelength regions of interest. As RaF<sup>(+)</sup> is a significantly heavier system, its rotational and vibrational constants scale favourably when considering its potential for rovibrational cooling with laser light.

A future experiment aiming to search for signatures of an electron electric dipole moment (eEDM) in RaF may utilize either optical-cycling or buffer-gas cooling. While cryogenic buffer-gas cooling is an established technique in molecular eEDM searches [22–24], the technical developments required for substituting a room-temperature cooler-buncher at an RIB facility to a cryogenic one raise the necessity for a detailed investigation into whether optical pumping with spectral shaping can be pursued instead.

### 3. Computational Methods

Two sets of calculations were performed for both RaF<sup>+</sup> and RaH<sup>+</sup>; 1) two-component all-electron calculations within the molecular-mean-field X2C quasirelativistic framework (see [25,26] for details on the X2C approach) 2) scalar-relativistic calculations using 78-electron energy-consistent ECP on Ra and 2-electron ECP on F [27]. The scalar-relativistic calculations were performed using the MOLPRO 2019.2.0 program package, while the X2C calculations were performed using the DIRAC19 program package [28].

#### 3.1. X2C Quasirelativistic Calculations

In the X2C calculations, the basis set [28s26p18d12f], analogous to the one used in Refs. [29,30], was used for Ra, while the uncontracted ANO-RCC basis set [14s9p4d] by Roos and co-authors was used for F and the correlation-consistent basis set cc-pVTZ [5s2p1d] by Dunning, contracted to [3s2p1d], was used for H. A Gaussian nuclear model was employed in all calculations, with nuclear Gaussian exponents  $1.310 \times 10^8$  (Ra),  $5.355 \times 10^8$  (F) and  $21.25 \times 10^8$  (H).

Firstly, DHF calculations of the lowest-by-energy closed-shell configuration of the singly charged cations RaF<sup>+</sup> and RaH<sup>+</sup> were performed. Afterwards, Kramers-restricted generalised active space CI (GAS-CI) calculations (for details on the GAS-CI scheme see Ref. [31]) were performed, accounting for correlations of 16 electrons in RaF<sup>+</sup> and 10 electrons in RaH<sup>+</sup>. In the GAS-CI calculations, only single and double excitations were allowed from the ground-state closed-shell configuration to the space of virtual spinors which included for RaF<sup>+</sup> 120 Kramers pairs and for RaH<sup>+</sup> 150 Kramers pairs. Molecular symmetry  $C_{\infty v}$  was used in all the calculations; 3, 2 and 2 roots were calculated in the  $C_{\infty v}$  irreps corresponding to projections of total electron angular momenta  $\Omega = 0, 1$  and 2.

#### 3.2. Scalar-Relativistic ECP Calculations

For the scalar-relativistic ECP calculations, basis sets supplied with energy-consistent ECPs were used for both Ra (78 inner-core electrons are simulated by ECP) and F (2 inner-core electrons are included in ECP), while the basis set for F was also augmented by *d*-functions from the def2-QZVP basis set from MOLPRO basis set library. For H, *s*- and *p*-functions were taken from the def2-QZVP basis set from the MOLPRO basis set library.

As a result, the basis sets [15s14p8d4f], [4s5p3d] and [7s3p] were taken for Ra, F and H, respectively, in the ECP calculations. In all calculations, we started from DFT calculations with the B3LYP exchange-correlation potential of the closed-shell ground-state configuration of RaF<sup>+</sup> and RaH<sup>+</sup>. Molecular symmetry in all calculations was set to  $C_1$ ; the initial internuclear distance between Ra and F was taken to be equal to 4.0  $a_0$  and 4.38  $a_0$  for Ra and H. After the DFT calculations, a CASSCF calculation was performed, where the average energy of the two lowest singlet electronic states was minimized. For RaF<sup>+</sup> correlations between 6 valence electrons are accounted for by MCSCF method, while 10 electrons on the lowest energy MOs are frozen after the SCF/DFT step. Six valence electrons can occupy higher by energy four MOs (energetically following frozen 5 MOs), without restrictions to possible configurations, thus realizing minimal CASSCF scheme which allows us to capture in calculation excited electronic energies. An analogous

scheme of electron distribution over active MOs is used for  $\text{RaH}^+$ , where correlations between 10 valence electrons are accounted for (none of the electrons are frozen). In the last step, multireference internally contracted CI (micCI) calculations (as implemented in the MOLPRO package [32]) were performed. In the micCI calculations of  $\text{RaF}^+$ , the internal space consisted of 16 natural molecular orbitals with the greatest occupation numbers obtained from the CASSCF calculations, while for  $\text{RaH}^+$ , the internal CI space included 11 natural orbitals.

#### 4. Results and Discussion

Single-point X2C/GAS-CI calculations of  $\text{RaF}^+$  and  $\text{RaH}^+$  were firstly performed to estimate the relative energies of excited molecular levels and the positions of singlet and triplet states. In these calculations, the internuclear distances were taken to be approximately equal to the equilibrium internuclear distances of the ground electronic states of  $\text{RaF}^+$  and  $\text{RaH}^+$ . The results of the calculations are presented in Table 1. It can be seen that the properties of the excited states in  $\text{RaF}^+$  and  $\text{RaH}^+$  are distinctly different. In particular, the vertical excitation energies in  $\text{RaF}^+$  are almost two times higher than those in  $\text{RaH}^+$ , being in the range of  $10^5 \text{ cm}^{-1}$ . Such high transition frequencies indicate that laser-cooling techniques are inapplicable to both  $\text{RaF}^+$  and  $\text{RaH}^+$ , even in the case of quasideagonal FC-matrices for vibronic transitions between electronic states, as they lay far beyond the reach of state-of-the-art laser technology.

To elucidate the nature of chemical bonding in  $\text{RaF}^+$  and  $\text{RaH}^+$ , molecular geometry optimisation in the framework of the scalar-relativistic ECP approach was performed for both  $\text{RaF}^+$  and  $\text{RaH}^+$ ; the results are presented in Table 2. The data corroborate that chemical bonding is essentially different for  $\text{RaF}^+$  and  $\text{RaH}^+$ . It is worth noting that a number of scalar-relativistic correlation calculations of the electronic structure exists for lighter homologues of  $\text{RaH}^+$ , including  $\text{SrH}^+$  and  $\text{BaH}^+$  [33,34], and our previous experience with calculations of neutral  $\text{RaF}$  [3,30] show that, for the purpose of estimation of quality of calculation, the comparison of molecular parameters with the corresponding parameters in lighter homologues is justified.

The results of the scalar-relativistic calculations of  $\text{RaF}^+$  indicate that the excited states lie at about  $70 \times 10^3 \text{ cm}^{-1}$  over the ground electronic state, while in  $\text{RaH}^+$  the situation resembles that of the lighter homologues  $\text{BaH}^+$  and  $\text{SrH}^+$ , where electronic excitation energies are in the optical range. Additionally, the potential energy curves (PEC) of the excited electronic states are crucially different in the two cations. For  $\text{RaH}^+$ , the PEC of the first excited singlet state looks similar to the PEC of the ground state, having a well-defined minimum and harmonic vibrational quanta in the order of a few hundred  $\text{cm}^{-1}$ , thus having the typical characteristics of a chemical bond. For  $\text{RaF}^+$ , the first excited singlet state is quasi-dissociative and resembles the bonding situation in a charge-neutral van der Waals complex. It must be emphasized, however, that the scalar-relativistic calculations for both  $\text{RaF}^+$  and  $\text{RaH}^+$  show considerably lower transition frequencies compared to the two-component X2C calculations.

The structure of the bonding molecular orbitals for the ground and excited electronic states in both  $\text{RaF}^+$  and  $\text{RaH}^+$  were also studied; the results are presented in Table 3.

The highest occupied molecular orbitals (HOMOs) in the ground electronic states of  $\text{RaF}^+$  (8.1) and  $\text{RaH}^+$  (5.1) are quite different. For  $\text{RaF}^+$  the HOMO is in fact the atomic fluorine orbital, which is expected for a strong ionic bond. In the case of the bond in  $\text{RaH}^+$ , which has a rather covalent character, the HOMO is distributed over both Ra and H. In the excited electronic state of  $\text{RaH}^+$ , averaged natural orbitals show that the electronic charge distribution remains similar to that in the electronic ground state. In the case of  $\text{RaF}^+$ , the charge distribution changes considerably from being centered on the fluorine atom into a covalent-type distribution. These points are also supported by Mulliken analyses of charge distribution on H and F, when going from the ground to excited electronic states: (1) in  $\text{RaH}^+$ , the charge on H in the ground electronic state is  $-0.28$ , and it becomes  $-0.21$  in

excited electronic state (2) in RaF<sup>+</sup>, the corresponding charges on F change from −0.59 to −0.36. Thus, a remarkable charge transfer takes place.

**Table 1.** Values of GAS-CI/X2C vertical excitation energies and projections of electronic orbital angular momentum on the internuclear axis  $l_z$  and electronic spin  $s_z$  for RaF<sup>+</sup> and RaH<sup>+</sup> for the internuclear distances  $4.16a_0$  and  $4.38a_0$  for Ra-F and Ra-H, respectively. Values of  $T_0$  are rounded to thousands of  $\text{cm}^{-1}$  to emphasize the suggested accuracy of the calculations.

RaF <sup>+</sup>				RaH <sup>+</sup>			
$\Omega$	$T_0$	$l_z$	$s_z$	$\Omega$	$T_0$	$l_z$	$s_z$
0	0	−0.0002	0.0002	0	0	0.0023	−0.0023
0	$114 \times 10^3$	−0.0243	0.0243	0	$55 \times 10^3$	−0.0119	0.0119
1	$114 \times 10^3$	0.9768	0.0232	1	$55 \times 10^3$	0.0103	0.9897
0	$114 \times 10^3$	0.0236	−0.0236	0	$58 \times 10^3$	0.0163	−0.0163
2	$118 \times 10^3$	0.9998	1.0002	2	$64 \times 10^3$	1.0055	0.9945
1	$118 \times 10^3$	0.0003	0.9997	2	$66 \times 10^3$	2.0030	−0.0030
2	$125 \times 10^3$	−0.0215	2.0215	1	$66 \times 10^3$	1.2694	−0.2694

**Table 2.** Results of the molecular geometry optimisation for the ground and excited electronic states for RaF<sup>+</sup> and RaH<sup>+</sup> in scalar-relativistic ECP calculations. The equilibrium distance  $R_e$  is in Å, adiabatic transition energies  $T_e$  and harmonic vibrational quanta are in  $\text{cm}^{-1}$ . For comparison, the data from [33,34] for molecular constants of SrH<sup>+</sup> and BaH<sup>+</sup> are provided.

	RaF <sup>+</sup>		RaH <sup>+</sup>		SrH <sup>+</sup>		BaH <sup>+</sup>	
State	X( <sup>1</sup> Σ)	A( <sup>1</sup> Σ)	X( <sup>1</sup> Σ)	A( <sup>1</sup> Σ)	X( <sup>1</sup> Σ)	A( <sup>1</sup> Σ)	X( <sup>1</sup> Σ)	A( <sup>1</sup> Σ)
$R_e$	2.20	17.98	2.32	2.98	2.073 <sup>1</sup>	2.608 <sup>1</sup>	2.177 <sup>1</sup>	2.913 <sup>1</sup>
					1.97 <sup>2</sup>	2.47 <sup>2</sup>	2.079 <sup>2</sup>	2.719 <sup>2</sup>
$\omega_e$			1251	542	1264 <sup>1</sup>	678 <sup>1</sup>	1353 <sup>1</sup>	515 <sup>1</sup>
$T_e$				21,791		24,027 <sup>1</sup>		23,365 <sup>1</sup>
						23,972 <sup>2</sup>		

<sup>1</sup> data from [33]; <sup>2</sup> data from [34].

**Table 3.** MO-LCAO expansion of the averaged natural molecular orbitals in ground and excited <sup>1</sup>Σ states of RaF<sup>+</sup> and RaH<sup>+</sup>, with the corresponding occupation numbers. Only expansion coefficients larger than 0.3 are provided.

State	N	Occ	RaF <sup>+</sup>	N	Occ	RaH <sup>+</sup>
X ( <sup>1</sup> Σ)	8.1	2.0	(0.44482 $p_z$ + 0.43291 $p_z$ )(F)	5.1	2.0	(−0.34524s + 0.32983s)(Ra) + (0.31941s)(H)
A ( <sup>1</sup> Σ)	8.1	1.5	(0.26669 $p_z$ )(Ra) + (0.46247 $p_z$ + 0.46855 $p_z$ )(F)	5.1	1.5	(0.42396s)(H)
	9.1	0.5	(0.34216s − 0.32604s − 0.60611s + 0.98934s)(Ra)	6.1	0.5	(0.32950s − 0.31464s − 0.56286s + 0.99801s)(Ra)

### 5. Conclusions

An investigation of the electronic structure of the RaF<sup>+</sup> and RaH<sup>+</sup> molecular cations was performed to explore the prospect of direct rovibrational laser cooling. Additionally, the nature of chemical bonding in both compounds was studied for the ground and excited electronic states. It is concluded that for both RaF<sup>+</sup> and RaH<sup>+</sup>, the application of direct laser-cooling techniques appears unfeasible due to the high transition energies that lie beyond the capability of modern state-of-the-art laser technology. However, according to the data from the Table 2 we see a trend in scalar-relativistic calculations in series of (Sr- > Ba- > Ra)H<sup>+</sup> compounds, that excitation energies of X- > A transitions are gradually decreasing. However, X2C calculations, where spin-orbit effects are accounted for, show higher excitation energies than these in scalar-relativistic calculations for RaH<sup>+</sup>. Thus, more sophisticated calculations of the electronic structure of RaH<sup>+</sup> utilizing a basis set extended to higher harmonics and a larger spinor space for electron excitation in MRCI would be of

interest, especially combined with similar calculations of neutral RaH. In the latter case, it would be interesting to see deviation from simple “one-electron-over-closed-shell” picture, as possible low-lying states connected with excitation with electron from closed shell could be rather close in energy to the states generated by excitation of the valence electron.

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