

# EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

## Proposal to the ISOLDE and Neutron Time-of-Flight Committee

### Collinear resonance ionization spectroscopy of RaF molecules

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**Abstract:** The low-energy molecular structure of  $^{225,226}\text{RaF}$  molecules will be studied using collinear resonance ionization spectroscopy. These molecules have been proposed as highly-sensitive systems for studies of fundamental symmetries. However, all of their spectroscopic properties are unknown experimentally. Our measurements will provide, for the first time, the excitation energy of the first excited state as well as a measurement of its ionization potential. These results are crucial to test the reliability of *ab initio* quantum-chemistry calculations developed for these systems, and are essential to establish the laser-cooling scheme of RaF molecules for future studies of fundamental symmetries.

**Requested shifts:** 18 shifts (without protons) distributed in 1 run.



# 1 Motivation

Diatomic molecules provide suitable physical systems for studies of fundamental symmetries with unprecedented sensitivity [1–7]. The possibility of extending commonly used laser-cooling techniques in atoms to molecular systems have opened a new research area in high-precision studies [5, 6, 8–11]. Cold molecules provide exceptional opportunities for studies in quantum computation [12], chemical dynamics [13] as well as for exploring physics beyond the standard model [6, 9, 10]. However, due to the vibrational and rotational degrees of freedom, molecular systems often possess complex structures. This makes identifying closed-cycle transitions suitable for laser cooling considerably more challenging when compared to atomic systems. Furthermore, experimental knowledge of spectroscopic properties in molecules is scarce, and in most of the cases, quantum chemistry calculations constitute the only source of information. Since the experimental demonstration of laser cooling of SrF molecules [5, 6], a great deal of experimental and theoretical attention has been focused on the study of fluoride molecules such as CaF [14], MgF [15, 16], TiF [17, 18], BaF [19], HfF [9], and RaF [20–22]. The latter, RaF, predicted to be particularly sensitive to parity-violating effects [20, 21] as well as for electron electric dipole moment (EDM) searches [21–23]. This molecule is predicted to have one of the largest nuclear-spin-dependent P-odd interaction constant,  $W_a$  [20], with a singular electronic structure appropriated for direct laser cooling. However, only theoretical predictions are available for this molecule, and all of its spectroscopic parameters are experimentally unknown. Here, we propose to perform collinear resonance ionization spectroscopy experiments on the  $^{225}\text{RaF}$  and  $^{226}\text{RaF}$  molecules. These experiments will provide the first experimental determination of the excitation energy of the low-lying excited states of RaF molecules in addition to its ionization potential. These experimental parameters are crucial to test the validity of *ab initio* quantum-chemistry calculations developed for these systems [20–22], and are essential to establish the laser-cooling scheme of RaF molecules for future studies of fundamental symmetries in this system [20–23].

## 2 Experimental details

The Collinear Resonance Ionization Spectroscopy (CRIS) experiment at ISOLDE [24] offers a unique opportunity to perform the required measurements.  $\text{RaF}^+$  molecules can be produced at ISOLDE, and the high sensitivity of the CRIS technique, combined with the possibility of using both broadband and narrowband lasers, allows us to rapidly explore large frequency spaces. Monofluoride molecules possess a relatively simple structure [5, 6], which allows the application of the CRIS experimental method using a two-step ionization scheme. The predicted level scheme for RaF is shown in Figure 1.

The HRS separator will be used in combination with the cooler-buncher ISCOOL. Bunches of singly-ionized molecules ( $\text{RaF}^+$ ) will be redirected into the CRIS beam line. At CRIS, the molecules will be neutralized in-flight by using a charge-exchange cell (CEC) loaded with Na vapour (ionization potential of 5.14 eV). As the ionization energy of the RaF molecule is estimated to be around 5 eV, a relatively high cross section of neutralization into the RaF ground state is expected by using a sodium vapour [25]. Afterwards, the neutralized RaF molecules, are overlapped with two laser beams in a collinear geometry in an UHV interaction region (1.2 m). A broadband laser can be used to resonantly excite the transition of interest, and subsequently, a high-power 355-nm laser pulse is used to ionize the RaF molecule into a  $\text{RaF}^+$  state. The resonantly-ionized molecules are then separated from the non-interacting neutral molecules via electrostatic deflector plates and detected by an MCP particle detector.

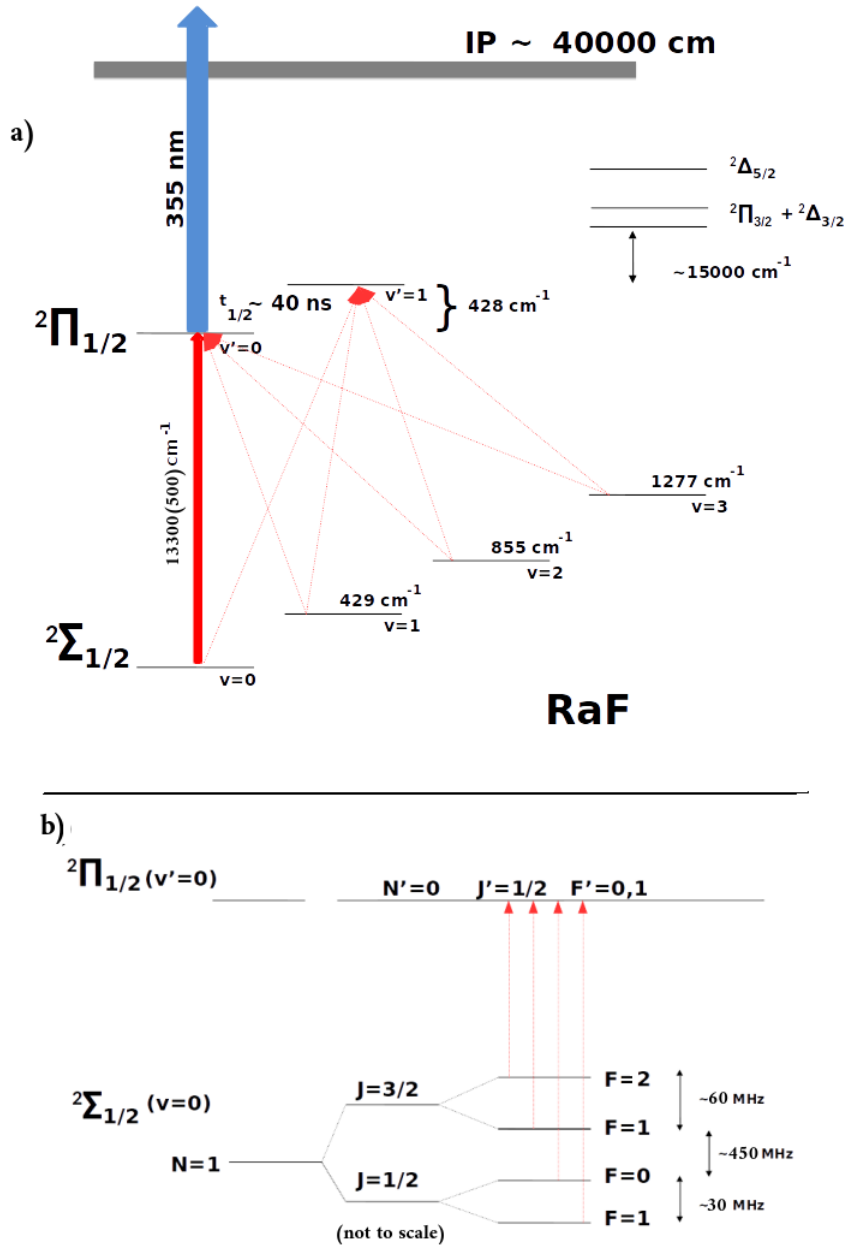


Figure 1: a) Resonance ionization scheme predicted for the study of RaF molecules. The arrows indicate transitions of interest for the RaF cooling scheme [20,21,23]. b) Example of the splitting for the rotational energy level  $N = 1$ . Each rotational level splits in  $J = N \pm S$  states, with  $S = 1/2$  the spin of the unpaired electron. For the case of  $^{226}\text{RaF}$ , the nuclear spin of  $^{19}\text{F}$  ( $I = 1/2$ ) splits each state  $J$  into the hyperfine levels  $F = J \pm 1/2$ . Only rough estimations are presented for the hyperfine splittings.

Molecule	Half life	Yield (ions/s)	Target	Shifts
$^{222}\text{RaF}^+$	38 s	$2 \times 10^6$	$\text{UC}_x$	–
$^{225}\text{RaF}^+$	15 d	$> 10^5$	$\text{UC}_x$	2
$^{226}\text{RaF}^+$	1600 y	$> 10^6$	$\text{UC}_x$	15
$^{138}\text{BaF}^+$	stable	$> 10^6$	$\text{UC}_x$	1

Table 1: Reported yields and beam time request. Beam intensities are estimated from measurements of  $^{222}\text{RaF}^+ = 2 \times 10^6$  ions/s [27] and more recently measurements of  $^{224}\text{RaF}^+ = 2.5 \times 10^5$  ions/s [26].

*Ab initio* quantum chemistry calculations predict the first excited state at  $13300(1200)$   $\text{cm}^{-1}$  [20, 23]. Improved calculations reduce this uncertainty to below  $500$   $\text{cm}^{-1}$ . The relatively low ionization energy predicted for this molecule allows the application of a two-step laser ionization (Figure 1). While fixing the second non-resonant ionization step at  $355$  nm, the first step will be scanned around  $13300(500)$   $\text{cm}^{-1}$ , which is equivalent to wavelengths in the range  $724 - 781$  nm.

## 2.1 Laser setup

The proposed resonance ionization schemes for the study of RaF molecules is shown in Figure 1. The scanning range from  $724$  nm to  $781$  nm can be covered by two different laser systems; a high power broadband dye laser ( $30$  GHz  $\equiv 1$   $\text{cm}^{-1}$ ) will be used to provide the scanning step in the range  $724$ - $760$  nm. Wavelengths from  $760$  to  $781$  nm can be covered by a grating TiSa laser system with a linewidth of  $2$  GHz ( $\equiv 0.07$   $\text{cm}^{-1}$ ). The non-resonant ionization step,  $355$  nm, will be obtained from a high-power Nd:YAG laser ( $100$  Hz), recently installed adjacent to the CRIS beamline.

## 3 Beam-time request

Relatively large yields for  $\text{BaF}^+$  and  $\text{RaF}^+$  molecules have been observed at ISOLDE [26]. These molecules can be produced by surface ionization with a  $\text{UC}_x$  target. Values for previously reported and expected yields are shown in Table 1. To account for the population of different molecular states and additional background sources, **a total efficiency is estimated as 0.0005 %**. This efficiency value was obtained by assuming a total transport efficiency of  $30$  %, a particle detection efficiency of  $80$  %, a laser ionization efficiency of  $2$  %, and a neutralization factor of  $0.001$  into the molecular state of interest. This factor takes into account that the RaF molecules are created in different vibrational and rotational states.

The details of the beam production and the required shifts for this experimental proposal are summarized in Table 1. The motivation for the proposed measurements and beam time request are explained in the following sections.

### Optimizing the setup with $^{138}\text{BaF}$

As the energy levels and ionization energy of the BaF molecule are experimentally known [28, 29], this molecule can be used as a reference to test and optimize the experimental setup using the laser ionization scheme  $860$  nm +  $355$  nm [28, 29]. The resonance ionization scheme for this

molecule will be fully tested offline with the CRIS ablation ion source [30]. **1 shift** with the stable  $^{138}\text{BaF}^+$  is required.

## Excitation energy of $^{226}\text{RaF}$

For a  $\text{RaF}^+$  beam of  $10^6$  ions/s, about 5 count/s would be obtained on resonance assuming a total efficiency of 0.0005%. Background factors from collisional and non-resonant ionization better than  $1:10^5$  are commonly achieved during CRIS experiments. Considering a pessimistic background factor of  $1:10^4$  for this case (non-resonant background with  $\sim 100$  count/s), once the laser is at the resonance position, a resonance peak would be observed with  $3\sigma$  above background, in about 65 seconds. Thus, the time for scanning a region of  $100\text{ cm}^{-1}$  ( $\equiv 3000$  GHz) with steps of 6 GHz every 65 seconds ( $\approx 0.1$  GHz/s) is 8 hours (1 shift). After every  $100\text{ cm}^{-1}$  an optimization of the laser system is required. Assuming interruptions of 30 minutes every 8 hours for laser optimization, the total time required to scan a region of  $1000\text{ cm}^{-1}$  is estimated to be 85 hours (**10.6 shifts**). Once the resonance peaks corresponding to the vibrational ground state ( $\nu = 0$ ) and rotational state ( $N = 1$ ) have been identified within a range of 30 GHz, a narrowband scan with a scanning speed of 0.3 MHz/s can be performed in 28 hours ( $\sim$  **3.5 shift**).

## Ionization potential of $^{226}\text{RaF}$

Fixing the first step at the resonance position [31], the second step can be scanned around  $26700(1000)\text{ cm}^{-1}$  ( $\equiv 360\text{-}390\text{ nm}$ ) by using the doubled light of a broadband dye laser system. To find the ionization potential, a scanning speed of  $0.1\text{ cm}^{-1}/\text{s}$  can be used. Considering the optimization of the laser system every  $100\text{ cm}^{-1}$ , a  $1000\text{ cm}^{-1}$  range can be scanned in **1 shift**.

## Hyperfine structure of $^{225}\text{RaF}$

Diatomic molecules containing isotopes of nuclear spin  $I \neq 0$  were proposed to be highly sensitive to the nuclear anapole moment and parity violation effects [4]. As there is no contribution from  $^{226}\text{Ra}$  ( $I = 0$ ) to the molecular hyperfine levels, measurements with  $^{225}\text{Ra}$  ( $I = 1/2$ ) can provide information on the interaction between electrons and nucleus in the  $^{225}\text{RaF}$  molecule. After determining the transition energy for the first excited state of  $^{226}\text{RaF}$ , the transition energy for  $^{225}\text{RaF}$  can be predicted within a range lower than 100 GHz. Scanning such a range with both broadband and narrow band lasers can be performed in **2 shifts**. From these measurements the components of the hyperfine tensor for  $^{225}\text{Ra}$  nucleus can be extracted, which can be compared with the available theoretical calculations [21]. Moreover, these parameters are important for possible future studies of nuclear spin-dependent parity violation effects with RaF molecules [4].

**Summary of requested shifts:** 18 shifts (without protons) are required, distributed in one run.

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# Appendix

## DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the	Availability	Design and manufacturing
CRIS	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification
[Part 1 of experiment/ equipment]	<input type="checkbox"/> Existing	<input type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
	<input type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
[Part 2 of experiment/ equipment]	<input type="checkbox"/> Existing	<input type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
	<input type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
[insert lines if needed]		

HAZARDS GENERATED BY THE EXPERIMENT (if using fixed installation:) Hazards named in the document relevant for the fixed CRIS installation.

Additional hazards: no additional hazards

Hazards	[Part 1 of experiment/ equipment]	[Part 2 of experiment/ equipment]	[Part 3 of experiment/ equipment]
<b>Thermodynamic and fluidic</b>			
Pressure	[pressure][Bar], [volume][l]		
Vacuum			
Temperature	[temperature] [K]		
Heat transfer			
Thermal properties of materials			
Cryogenic fluid	[fluid], [pressure][Bar], [volume][l]		
<b>Electrical and electromagnetic</b>			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	<input type="checkbox"/>		
Capacitors	<input type="checkbox"/>		



<b>Ionizing radiation</b>			
Target material [material]			
Beam particle type (e, p, ions, etc)			
Beam intensity			
Beam energy			
Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	<input type="checkbox"/>		
• Open source	<input type="checkbox"/>		
• Sealed source	<input type="checkbox"/> [ISO standard]		
• Isotope			
• Activity			
Use of activated material:			
• Description	<input type="checkbox"/>		
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope			
• Activity			
<b>Non-ionizing radiation</b>			
Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300 MHz)			
<b>Chemical</b>			
Toxic	[chemical agent], [quantity]		
Harmful	[chem. agent], [quant.]		
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chem. agent], [quant.]		
Corrosive	[chem. agent], [quant.]		
Irritant	[chem. agent], [quant.]		
Flammable	[chem. agent], [quant.]		
Oxidizing	[chem. agent], [quant.]		
Explosiveness	[chem. agent], [quant.]		
Asphyxiant	[chem. agent], [quant.]		
Dangerous for the environment	[chem. agent], [quant.]		
<b>Mechanical</b>			

Physical impact or mechanical energy (moving parts)	[location]		
Mechanical properties (Sharp, rough, slippery)	[location]		
Vibration	[location]		
Vehicles and Means of Transport	[location]		
<b>Noise</b>			
Frequency	[frequency],[Hz]		
Intensity			
<b>Physical</b>			
Confined spaces	[location]		
High workplaces	[location]		
Access to high workplaces	[location]		
Obstructions in passageways	[location]		
Manual handling	[location]		
Poor ergonomics	[location]		

Hazard identification:

Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): [make a rough estimate of the total power consumption of the additional equipment used in the experiment]