Ion neutralisation mass-spectrometry route to radium monofluoride (RaF)

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We have shown recently that radium monofluoride (RaF) can be considered a promising open-shell molecular candidate which is well-suited for a wealth of tests on physics beyond the standard model. This is a result of the following properties of the RaF system. The molecules is proposed to be amenable for direct cooling with lasers1 and it shows favourable relativistic enhancement factors2, a particular open shell structure with lasers1 and it shows favourable relativistic enhancement factors2, with lasers1, a particular open shell structure with lasers1, a particular open shell structure with lasers1, with lasers1 and it shows favourable relativistic enhancement factors2, a particular open shell structure2, a particular open shell structure2, a particular open shell structure2, a particular open shell structure2, and nuclear octapole deformations for certain radium isotopes4–6. No experimentally obtained information on molecular parameters of diatomic RaF in any of its charge states appears to be available in the open literature and thus quantum chemically computed data are the only source of information.

Herein we propose a route to gain first access to information on neutral radium monofluoride via intermediate production of RaF+ which is subsequently neutralised by charge exchange in collision with a suitable chosen collision gas or by interaction with surfaces that provide the adequate work function for an iso-enthalpic electron transfer. As the degree of electron-transfer-induced dissociation should be kept at a minimum, favourable Franck–Condon factors (FCFs) for neutralisation are required. This is related to one of the general prerequisites for molecules to serve as potential candidates for being cooled with lasers, which has recently been successfully demonstrated for the molecule SiF4. According to our classification scheme of molecules that should be amenable to being cooled directly with lasers1, changes in occupation of non-bonding orbitals disturb the molecular structures of diatomic molecules only to a small degree, such that favourable FCFs can be expected in these transitions. As similar considerations hold for the efficiency of neutralisation-reionisation and charge-reversal transitions in molecular systems, which have found a wealth of applications10,11, the same classification can also be applied to identify particular suitable compounds for charge-state changing transitions, which can be light-induced or collision-induced.

As the lowest energy ionisation step for radium monofluoride can be expected to be due to the removal of an electron in a non-bonding orbital of this heavy elemental compound (case 1 and 3 in Ref.1), the corresponding closed-shell RaF+ in its ground state is expected to feature quite similar bond length and vibrational frequencies. In this brief note, we demonstrate with explicit four-component Fock-Space Coupled-Cluster (4c-FSCC) calculations using the Dirac program package12 that this indeed true. Details of these computations are described in the supplementary material.

RaF+ can in principle be formed in reactive collisions of radium ions with a suitable fluorine containing compound. This expectation is fueled by the work of Armentrout and Beauchamp13, who generated UF+ for instance by reaction of U+ with methyl fluoride (CH3F) to yield the desired molecular cation in an exothermic process, such that cross sections decreased with increasing collision energy. Alternatively, reaction of uranium ions with tetrafluoro-silane (SiF4) afforded UF+ in an endothermic process, such that cross sections increased with increasing collision energy. These and other fluorinating agents such as SF6, PF5 and NF3 should yield also the radium monofluoride monocation, with the choice of reagent offering tunability in this respect. According to the computed dissociation energies (see Table1), SiF4 should provide access to RaF+ in an endothermic process, whereas the analogous reaction with CF4 is expected to proceed almost thermoneutral.

To assess the viability for an undissociated neutralisation of RaF+ we computed the potential energy curve of electronic ground state RaF+, compared this curve to the one of neutral RaF in its electronic ground state and estimated the FCFs for transition to the lowest vibrational

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TABLE I. Estimated molecular spectroscopic parameters for the electronic ground state $^1\Sigma_0$ of $^{226}$RaF$^+$ from FS-CCSD calculations (see supplementary material for details) and comparison to previously calculated parameters of neutral RaF.

| $^1\Sigma_0$ | $^2\Pi_{1/2}$ | $^2\Pi_{1/2}$ | $^2\Sigma_{1/2}$ | $^2\Sigma_{1/2}$ |
|--------------|---------------|---------------|----------------|----------------|
| R$_a$/a$_0$  | $\omega_e$/cm$^{-1}$ | $\omega_r$/cm$^{-1}$ | $\Delta_e$/cm$^{-1}$ | $\Delta_r$/cm$^{-1}$ |
| 4.14 | 502 | 4.51 | 4.00 | this work |
| 4.29 | 428 | 4.24$^a$ | 1.33 | Ref. [2] |
| 4.24 | 432 | 3.13 | 1.40 | Ref. [1] |
| 4.29 | 431 | 4.26$^a$ | 0 | Ref. [2] |
| 4.24 | 428 | 3.21 | 0 | Ref. [1] |

$^a$) this work

states of the neutral in the electronic ground state. The predicted molecular parameters are given in Table I along with the data computed previously for RaF.

According to the data presented in Table I, favourable FCFs exist for the neutralisation step of RaF monocation (anharmonic Morse oscillator estimates for the FCFs are 0.49 (0 $\rightarrow$ 0); 0.34 (0 $\rightarrow$ 1); 0.12 (0 $\rightarrow$ 2) and imply a nearly quantitative FC transition to bound levels of the neutral, even for vibrational temperatures of 3000 K in RaF$^+$. Charge-exchange cells with selected alkali vapours are routinely used to neutralise low-energy ions beams with up to unit efficiency $^{14}$. As the electron affinity of RaF$^+$, and conversely the ionisation energy of neutral RaF, are computed to be about 5 eV, collision with sodium vapour ($I = 5.14$ eV) can facilitate almost thermoneutral charge exchange between RaF$^+$ and sodium with comparatively large cross sections for yielding RaF in its electronic ground state. Interestingly, the lowest excited doublet state of RaF has an almost identical potential energy curve as the electronic ground state and thus similarly favourable FCFs for the neutralisation process. As atomic caesium features an ionisation energy of about $I = 3.89$ eV, a collision with a vapour of caesium can provide direct access to RaF in the $^2\Pi_{1/2}$ excited state in a slightly endothermic reaction. The corresponding fluorescence to the electronic ground state might then be monitored to give first indications of the properties of neutral RaF being produced in this collision. This might also be considered as the first step towards an optical cooling of RaF with lasers. If a laser beam is aligned along the molecular beam of neutral RaF, a more detailed investigation (collinear spectroscopy, see for instance $^{14, 15}$) of molecular properties can be facilitated. An indirect detection of RaF can be achieved by subsequent collisional reionisation of RaF in a neutralisation-reionisation type mass spectrometry experiment ($^+\text{NRMS}^+$). This type of experiment could for instance be realised at CERN’s Isotope Separator On Line (ISOLDE) facility: the typical yield of Ra$^+$ achieved there is about $10^7$ ions/µC $^{16, 17}$. According to $^{17}$ a beam of $^{222}\text{RaF}^+$ was also observed in July of 2007 with an intensity of $2 \cdot 10^6$ ions/µC while bombarding a uranium carbide target with high-energy protons. Taking for an estimate of the RaF$^+$ beam intensity 1/10 of the yield of the corresponding Ra isotope from the database $^{16}$, one can expect an intensity of $^{225, 226}\text{RaF}^+$ of the order $10^7$ ions/µC (or $10^7$ ions/s for a typical proton beam intensity of 1 µA).

To summarise the possible route towards a molecular beam of neutral radium fluoride: Charged radium isotopes formed in spallation experiments are reacted with a fluorine containing collision or buffer gas to afford RaF$^+$, which can subsequently be mass selected and neutralised in a collision with a vapour of sodium or a suitable surface. If a material with sufficiently low work function exists, generation of RaF in an electronically excited state is also possible, such that RaF can be identified by emission of a fluorescence photon, as the initiation of the first cycle in a cooling procedure with lasers. This scheme should give access to neutral RaF, which – after cooling and stopping either with lasers or by Stark deceleration – can be subject to a detailed search for physics beyond the standard model.

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