

Ionization potential of radium monofluoride

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The ionization potential (IP) of radium monofluoride (RaF) was measured to be 4.969(2)[10] eV, revealing a relativistic enhancement in the series of alkaline earth monofluorides. The results are in agreement with a relativistic coupled-cluster prediction of 4.981(7) eV, incorporating up to quantum electrodynamics corrections. Using the same computational methodology, an improved calculation for the dissociation energy (D_0) of 5.54(5) eV is presented. This confirms that RaF joins the group of diatomic molecules for which $D_0 > \text{IP}$, paving the way for precision control and interrogation of its Rydberg states.

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The ionization potential (IP), defined as the minimum energy required to release a bound electron, is a fundamental property of atoms and molecules, and is important in chemistry and physics. The IP is central to revealing rigorous and

intuitively appealing interrelationships among all electronic structural properties of atoms and molecules [1]. Electronic states of these systems can be arranged into series, which differ in their principal quantum number n and state energy. The energy of these states within each series increases with n and eventually converges at the IP.

Due to the highly nonlinear scaling of atomic and molecular properties with n , states with $n \gg 1$ can exhibit remarkable properties when compared to their ground states. These “Rydberg states” can have micrometer-sized atomic radii, extended lifetimes, and extremely large transition dipole moments, thousands of times larger than those for their low-lying (low- n) states [2]. These exceptional characteristics make Rydberg states prominent systems for quantum computing and simulation [3], precision measurements [4], and the

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investigation of long-range interactions due to their high sensitivity to external electric fields and photon absorption.

For the majority of diatomic molecules, however, the dissociation energy (D_0) lies lower in energy than the IP. This severely limits the ability of experiments to precisely study and manipulate their high-lying Rydberg states, as the molecules can fragment following predissociation on short (nanosecond) timescales. The short lifetimes of Rydberg states in these molecules intrinsically limit the attainable resolution of experiments attempting to measure them, preventing precision investigations of the properties of the molecular ion core. A notable exception to this trend, with $D_0 > \text{IP}$, is BaF, which has been an important system for the investigation of molecular Rydberg states [5,6]. More recent experiments have leveraged this property to realize high-resolution studies, enabling detailed insights into the nature of molecular Rydberg states in BaF [7].

Molecules containing isotopes of radium have been proposed as being promising systems in which to study the fundamental symmetries of the Universe [8–11], particularly in the hadronic sector of the standard model, where the rare octupole deformation of certain radium isotopes significantly boosts their sensitivity to P , T -violating phenomena [12]. An important example is the radium monofluoride (RaF) molecule, which was theoretically predicted [8] and later experimentally confirmed to be directly laser-coolable [13–15]. Although measurable progress has been made in investigating the spectroscopic properties of RaF [10,16], numerous critical quantities remain undetermined and the molecule has yet to be cooled and slowed to a sufficient degree to enable trapping for precision measurements. Furthermore, performing accurate calculations on atoms and molecules containing heavy elements requires sophisticated theoretical methods that have to be specifically tailored to account for relativistic and quantum electrodynamics (QED) effects that scale rapidly with atomic number in heavy elements. Experimental measurements play a crucial role in investigating the often dramatic influence of these contributions, providing critical information for both motivating and testing developments in cutting-edge theories, in addition to charting the evolution of chemical and physical properties toward the extremes of the periodic table.

Leveraging the unique properties of high-lying Rydberg states of RaF through manipulating them with external fields could enable the sensitive control of these molecules. This could allow a cryogenic buffer gas beam of them to be collimated and rapidly slowed to near the capture velocity of magneto-optical traps using Rydberg-Stark deceleration [17,18], setting the stage for precision measurements of CP violation. The efficient realization of such techniques, however, relies upon the condition that $D_0 > \text{IP}$, with both of these properties yet to be determined with sufficient precision in RaF.

Here, we demonstrate that RaF possesses a dissociation energy that exceeds its ionization potential. We report the first measurement of the IP of $^{226}\text{Ra } ^{19}\text{F}$, determined from the ionization threshold of its valence electron under multistep laser excitation using both two-step and three-step ionization schemes. The obtained value is compared with *ab initio* calculations performed within the relativistic coupled-cluster framework, corrected for higher-order effects, including QED

contributions. The same computational method is used to calculate its dissociation energy, resulting in an improved value and thus confirming that RaF indeed possesses the type of electronic structure for which $D_0 > \text{IP}$.

Experimental details. Bunches of $^{226}\text{Ra } ^{19}\text{F}^+$ were produced at the ISOLDE radioactive ion beam facility at CERN and studied with the collinear resonance ionization spectroscopy (CRIS) experiment. Details on the production of RaF molecules at ISOLDE can be found in Refs. [14,19]. Upon entering the CRIS beamline, the RaF^+ beam was neutralized in-flight after passing through a charge-exchange cell filled with a sodium vapor, where the neutral RaF molecules predominantly populated the $X \ ^2\Sigma^+$ electronic ground state [20]. The non-neutralized residual ions were deflected away, while the neutral bunches entered an ultrahigh-vacuum interaction region ($\approx 10^{-10}$ mbar), where they were collinearly overlapped with either two or three pulsed laser beams.

The ionization threshold was measured during two separate experiments. The ionization schemes for these are shown in Fig. 1(a). In both experiments, the first laser excited the $A \ ^2\Pi_{1/2}(v=0) \leftarrow X \ ^2\Sigma^+(v=0)$ transition of the RaF molecules [14], transferring molecules residing in multiple rotational states from the vibronic ground state [13]. In the first experiment, the second laser was used to ionize molecules directly from the $A \ ^2\Pi_{1/2}(v=0)$ state, constituting a two-step resonance ionization scheme. In the second experiment, the discovery of the higher-lying $E \ ^2\Sigma^+$ state [16] allowed a three-step resonance ionization scheme to be employed. This resulted in a significantly improved signal-to-background ratio as the superior pulse energy and beam quality of the ionization laser operating in its fundamental wavelength range increased the ionization efficiency while simultaneously decreasing the nonresonant background. Additional details on the laser setups for each experiment can be found in the Supplemental Material [21].

The wavelengths of the ionization lasers were scanned and the resulting RaF^+ molecular ions were deflected onto an ion detector. The ion count rate was monitored as a function of ionization laser wavelength. The total excitation energy delivered to each molecule by the lasers was determined by Doppler correcting the sum of the individual photon energies of the lasers in each ionization scheme. Two scans at each ionization laser wavelength were taken: one in which all lasers of each scheme were present in the interaction region and the other one where only the ionization laser was present such that any background resulting from the ionization laser could be accounted for. The ion rate was then determined as the difference between these two scans and linearly normalized with respect to the ionization laser power.

The resulting thresholds are shown in Figs. 1(c) and 1(d) for the two-step (teal squares) and three-step schemes (blue circles), respectively. Using the same method as presented in Ref. [22], the two sets of data were fit using a sigmoid function and the IPs were determined from the energy at which the ion rate saturates. This was done by determining the energy at which the tangent to the inflection point of the fitted sigmoid curves intersects the maximum ion rate, and its corresponding $\pm 1\sigma$ boundaries. The IPs and their statistical uncertainties are shown as the vertical dash-dotted lines and the narrow dark gray bands in Figs. 1(c) and 1(d). A

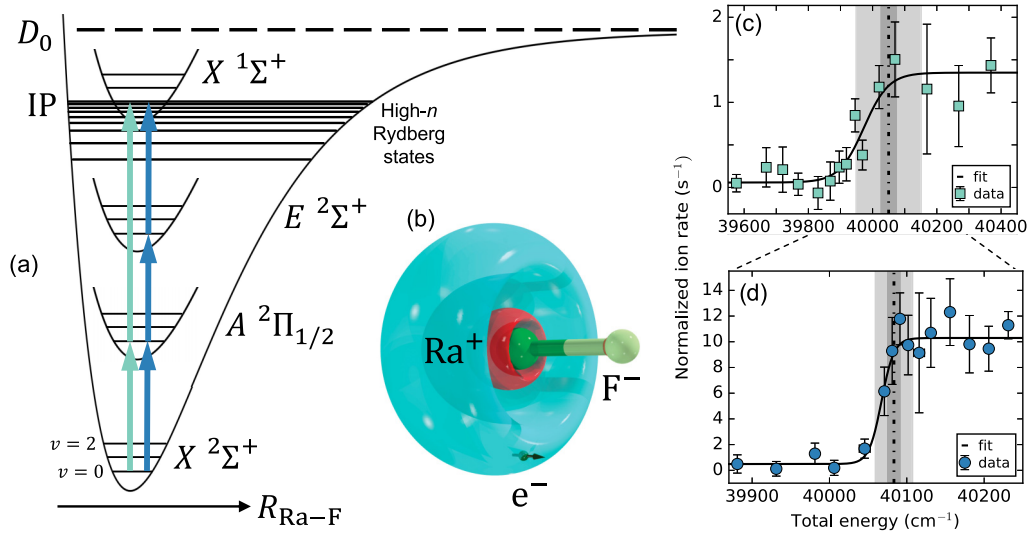


FIG. 1. (a) Molecular energy-level diagram for the electronic states in RaF and RaF^+ involved in the experiment with the IP and dissociation energy (D_0) shown. In addition, the two-step and three-step ionization schemes are denoted by a series of teal and blue upward arrows, respectively. (b) Orbital diagram of the $X^2\Sigma^+$ electronic ground state of RaF . Power-normalized, background-subtracted ion count rate as a function of total photon energy in $^{226}\text{Ra}^{19}\text{F}$ for the (c) two-step scheme (teal squares) and (d) three-step scheme (blue circles). The determined IPs are shown as vertical dash-dotted lines with their statistical and total uncertainties as dark and light gray bands, respectively.

systematic uncertainty from the fitting procedure is assigned by taking the energy difference between the inflection points of the curves and the extracted IPs. This is due to the lack of consistency in the literature regarding where the IP lies with respect to measured ionization thresholds. The total combined statistical and systematic uncertainties are shown as the wide light gray bands in Figs. 1(c) and 1(d). More details on the fitting and its justification can be found in the Supplemental Material [21]. The ionization threshold measured using the three-step scheme [Fig. 1(d)] can be seen to increase more sharply when compared to the two-step scheme [Fig. 1(c)]. This is due to the additional rotational angular momentum (J) selectivity introduced by having two sequential resonant excitations before the ionization step in the three-step scheme. This in turn reduced the number of high-lying Rydberg states populated by the ionization laser at energies below the IP, resulting in a sharper threshold. The ionization thresholds were determined to be $4.966(3)[10]$ and $4.970(1)[2]$ eV for the two-step and three-step schemes, respectively, with the statistical errors shown in parenthesis and the systematic errors shown in square brackets. More details on the fitting and its justification can be found in the Supplemental Material [21].

The majority of each molecular bunch was present in a shielded interaction region when the ionization process took place. However, a fraction of the molecules at the tail end of each bunch were outside of this region where stray fields are non-negligible. These molecules were gated out of the dataset as a conservative measure to negate any systematic downward shift of the observed thresholds resulting from the electric fields present. See the Supplemental Material [21] for more details on the time-of-flight gating.

As no significant change in the molecular equilibrium structure or vibrational quantum number occurs, the observed ionization thresholds from the $A^2\Pi_{1/2}$ and $E^2\Sigma^+$ states represent the adiabatic IP of RaF . The final experimental value

is given as $4.969(2)[10]$ eV, using the weighted standard deviation of the two-step and three-step scheme measurements to calculate the statistical error. The systematic errors from the two measurements were added in quadrature as the measurements were taken from separate independent experiments under different experimental conditions.

Computational method. Relativistic core-valence-correlating uncontracted Dyall basis sets [23,24] of varying cardinality, $\text{cvn}z$ ($n = 2-4$) augmented by a single layer of diffuse functions, were used ($\text{s-aug-cvn}z$). The coupled cluster with singles, doubles, and perturbative triples (CCSD(T)) method [25–27] was used to describe electron correlation and served as the baseline for subsequent corrections and uncertainty estimates. These corrections were evaluated at the CCSD(T) level or with full triples (CCSDT) using the appropriate Dyall basis sets with the bond lengths fixed at the respective equilibrium geometries of the neutral molecule and ion. The equilibrium bond lengths were obtained from the computed potential energy curves extrapolated to the complete basis set limit (CBSL) and are $2.236 \text{ \AA}$ for RaF ($X^2\Sigma^+$) and $2.162 \text{ \AA}$ for RaF^+ ($X^1\Sigma^+$), respectively. The CBSL extrapolation method employed the scheme in Ref. [28] for the Dirac-Hartree-Fock energy and the scheme in Ref. [29] for the correlation contribution. In the calculations, 49 electrons were correlated and the virtual space was cut off at $50 E_h$. In the calculation of the dissociation energy, the counterpoise approach to correct for the basis set superposition error [30] was also used.

To correct for the limited active space used, the difference between results obtained correlating 49 electrons with a $50 E_h$ cutoff and those obtained correlating all (97) electrons with a virtual space cutoff of $4000 E_h$ was calculated. In order to capture the full active space effect and to account for inner-core correlations, the all-electron quality basis set was used in the latter calculation. The more modestly sized dyall-cv3z and

dyall-ae3z basis sets were employed, as all-electron calculations were prohibitively computationally expensive at the 4z level. Furthermore, the possible lack of diffuse functions was accounted for by taking the difference between the d-aug-v4z and the s-aug-v4z results. The above corrections were calculated at a single geometry point (the ground-state equilibrium geometry) and added to the potential energy curves.

The effect of perturbative triple excitations on the CBSL level was determined to be 51 meV for the IP and 93 meV for D_0 . The effect of full triple excitations was evaluated to be around 1 meV for the IP and 3 meV for D_0 by comparing the values calculated at the CCSDT and CCSD(T) levels using the MRCC code [31,32]. These calculations were performed using the dyall.v3z basis sets, 16 correlated electrons, and a 10 E_h virtual cutoff. Higher-level excitations were not considered due to the very small difference between the CCSD(T) and CCSDT results.

In addition, the Breit and QED contributions were estimated. QED corrections were calculated using a development version of the DIRAC code [33,34]. Using this implementation in the molecular framework, two effective QED potentials were added variationally to the dc Hamiltonian. The QED correction itself was obtained from a single-point calculation at the equilibrium structure of neutral RaF. The Uehling potential [35] was employed for vacuum polarization and the effective potential of Flambaum and Ginges for the electron self-energy [36]. Our estimate of the size of the Breit effect relied on the fact that the electronic structure of RaF is very similar to that of Ra^+ and upon ionization the valence electron is removed from a σ orbital resembling a mildly perturbed atomiclike s orbital on Ra. Thus, the contribution of the Breit interaction to the IP and D_e of RaF was approximated by the effect calculated for the IPs of Ra^+ and Ra, respectively (direct calculations of molecular Breit contributions are challenging at present). These calculations were performed within the Fock-space coupled-cluster approach (DCB-FSCC), using the Tel Aviv atomic computational package [37]. The zero-point vibrational energy (ZPVE) correction for RaF and RaF^+ in the $^2\Sigma^+$ and $^1\Sigma^+$ states was deduced from their calculated vibrational frequencies of $\omega_e^{\text{RaF}} = 438 \text{ cm}^{-1}$ and $\omega_e^{\text{RaF}^+} = 518 \text{ cm}^{-1}$, respectively. Using these, the vibrationally corrected adiabatic IP is approximated as

$$\text{IP} = (E^{\text{RaF}^+} + \omega_e^{\text{RaF}^+}/2) - (E^{\text{RaF}} + \omega_e^{\text{RaF}}/2). \quad (1)$$

The ZPVE-corrected dissociation energy D_0 was obtained from the electronic dissociation energy D_e and the vibrational frequency of RaF (ω_e^{RaF}) using

$$D_0 = D_e - \omega_e^{\text{RaF}}/2. \quad (2)$$

The various higher-order corrections are added to the adiabatic CBS-DC-CCSD(T) IP and the final theoretical value was determined to be 4.981(7) eV, as shown in Table I. Using the same computational method, the dissociation energy D_0 of RaF was calculated to be 5.54(5) eV.

The uncertainty on the calculated IP and D_0 was evaluated through further computational investigation using similar procedures that were previously employed for various properties of both atoms and molecules [38–41]. The details of the

TABLE I. Experimental and calculated IP and D_0 of RaF.

Method	IP (eV)	D_0 (eV)
CBS-DC-CCSD	4.932 ^a	5.427
CBS-DC-CCSD(T)	4.983 ^a	5.520
+Augmentation	4.983	5.534
+Core corr.+ active space	4.989	5.530
+ ΔT	4.990	5.533
+Breit	4.988	5.531
+QED	4.981	5.540
Theoretical	4.981(7)	5.54(5)
Experimental	4.969(2)[10]	5.61(24) ^b

^aZPVE correction is included.

^bScaled from Ref. [14].

uncertainty treatment for both properties can be found in the Supplemental Material [21].

Discussion. Figure 2(a) shows experimental determinations of the IP of the group II monofluorides from CaF to RaF compared with theoretical calculations using the same method as for RaF described previously [42]. Experimental IP values measured using electron-impact [43–45] and laser spectroscopy methods [5,46] are shown as yellow diamonds and turquoise circles, respectively, with theoretical calculations shown as dark blue squares. The error bars for the laser measurements and theoretical predictions are smaller than the markers. Figure 2(b) shows the deviation, in units of standard deviations, between the theoretical predictions (dark blue squares) and experimental values (gray line). Where they

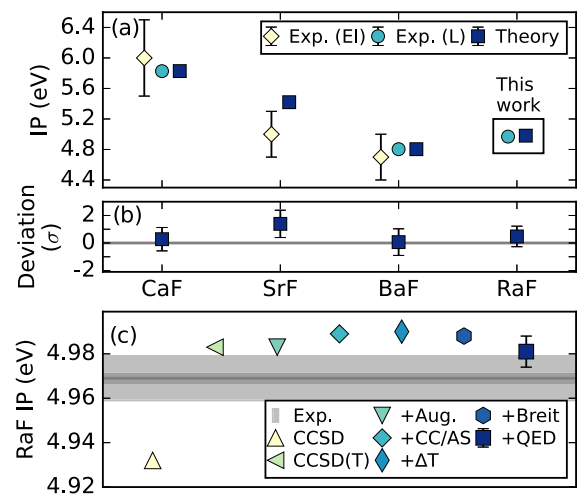


FIG. 2. (a) Comparison of predicted theoretical and measured values for the IP of group II monofluorides. Electron-impact [Exp. (EI)] [43–45] and laser [Exp. (L)] measurements [5,46] are denoted in the legend. The error bars for the laser measurements and theoretical predictions are smaller than the markers. (b) Deviation, in standard deviations, between the theoretical predictions (dark blue squares) and experimental values (gray line). (c) Comparison of experimental (Exp.) and theoretical values for the IP of ^{226}RaF for increasing computational sophistication (left to right). An uncertainty is shown only for the most accurate theoretical value. The thin dark gray band and thick light gray band correspond to the statistical and systematic uncertainties on the experimental value for the RaF IP.

exist, the experimental values used in the comparison are from laser spectroscopy methods using Rydberg states or ionization threshold measurements, owing to their higher precision. In SrF, where no laser measurements exist, an electron-impact measurement is used for comparison. Excellent agreement within 1 standard deviation is obtained for CaF, BaF, and RaF, whereas SrF agrees within 2 standard deviations. Figure 2(a) highlights the ability to determine the IP of RaF at a comparable or better precision than experiments on the homologues, despite the technical challenges imposed by its short-lived nature.

The IP of the group II monofluorides decreases progressively with increasing proton number, before increasing again in RaF. This increase in valence electron binding energy can be attributed to relativistic effects, which are significantly more pronounced in the heavier RaF. These effects result from the relativistic increase of the electron mass driven by the high velocity that bound electrons experience in atoms and molecules containing heavy elements [47]. This in turn spatially contracts orbitals with low angular momentum, which increases their binding energies [48,49]. The relativistic treatment required for correctly describing RaF is fully achieved in this study, yielding good agreement between theory and experiment as in the case of its homologues.

Figure 2(c) shows how the calculated IP for RaF evolves with an increasing level of computational sophistication. An agreement within 1 standard deviation is found between experiment and CCSD(T) theory that incorporates a complete basis set-extrapolation correction, nonperturbative triple excitations, and Breit and QED corrections. The QED correction surpasses all others in magnitude at the CCSD(T) level for the IP. However for D_0 , its magnitude is comparable to the basis set augmentation correction. This behavior is consistent with previous findings in atomic theory, where QED effects were shown to be of the same order as other post-CCSD(T) contributions [50]. This highlights the importance of accounting for them when undertaking precise calculations of the structure of atoms and molecules containing heavy elements and assists in attaining a theoretical uncertainty of just 7 meV for the IP of RaF.

Benchmarking the predictive power of molecular theory is crucial for the study of radioactive molecules, which is a prominent future avenue for precision tests of the standard model [11]. As most of the short-lived radioactive molecules of interest can only be made in small quantities at specialized facilities, none of their chemical properties are known experimentally even though knowledge of their chemical behavior is necessary to guide, or even enable altogether, their production and study [51,52]. Therefore, while the calculated IP of RaF is accurate even for predictions of lower sophistication in Fig. 2(c), the ability to reduce the theoretical uncertainty by including higher-order contributions, up to the QED level, is important to aid experiments attempting to perform the first spectroscopy of previously unexplored systems.

The previously calculated values of the ZPVE-corrected dissociation energy, D_0 , for RaF vary between 3.954 and 5.502 eV [8,20,53] with no corresponding uncertainties reported. Using the same computational method as for the IP, which achieves a more extensive and rigorous treatment of

higher-order contributions compared to previous studies, an improved calculation of the RaF D_0 equal to 5.54(5) eV is presented. This is in agreement with the RaF D_0 extracted from Morse potential fits in Ref. [14], provided that they are scaled by 1.55(6). Dissociation energy determinations from Morse potential fits use linear extrapolations that significantly underestimate the true dissociation energy in molecules where ionic bonding is important [54,55]. By taking the extrapolated D_0 values for CaF [56], SrF [57], and BaF [58], and comparing them to the true measured dissociation energies [59], the aforementioned scaling factor is obtained, which results in an RaF D_0 of 5.61(24) eV (using the $X^2\Sigma^+$ value from Ref. [14]). The resulting value and uncertainty of the computed D_0 , corroborated by the agreement between experiment and theory for the IP, confirms that RaF joins BaF in the class of diatomic molecules for which $D_0 > \text{IP}$.

Conclusion. The ionization potential of RaF was measured with the CRIS experiment at CERN-ISOLDE to be 4.969(2)[10] eV, through consistent observations of the ionization thresholds starting from two different excited electronic states. The IP was found to lie below the estimated dissociation energy, offering the possibility of accessing and utilizing Rydberg states in RaF, without loss due to predissociation. The stability of its Rydberg states opens up opportunities for employing Stark deceleration using their extremely large dipole moments (on the order of hundreds to thousands of debye). This technique could significantly improve molecular beam collimation or decelerate RaF molecules from 200 to under 10 m/s within 1 ms [17,18]. Such deceleration would enable subsequent laser cooling and trapping, setting the stage for high-precision measurements investigating the violation of fundamental symmetries in the hadronic sector with unprecedented sensitivity.

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Data availability. The data that support the findings of this article are openly available [60]; embargo periods may apply.

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