

Precision measurement of the first ionization potential of nobelium

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One of the most important atomic properties governing an element's chemical behaviour is the energy required to remove its least-bound electron, referred to as the first ionization potential. For the heaviest elements, this fundamental quantity is strongly influenced by relativistic effects which lead to unique chemical properties. Laser spectroscopy on an atom-at-a-time scale was developed and applied to probe the optical spectrum of neutral nobelium near the ionization threshold. The first ionization potential of nobelium is determined here with a very high precision from the convergence of measured Rydberg series to be 6.62621 ± 0.00005 eV. This work provides a stringent benchmark for state-of-the-art many-body atomic modelling that considers relativistic and quantum electrodynamic effects and paves the way for high-precision measurements of atomic properties of elements only available from heavy-ion accelerator facilities.

To date, 118 chemical elements are known [1]. Their chemical behaviour is mainly determined by the electronic configuration. This is subject not only to the Coulomb interaction, but, with increasing atomic number Z , also to large electron-electron correlations, quantum electrodynamic (QED) effects as well as relativistic effects. These relativistic effects influence the binding energy of the valence electrons, thus the chemical properties, as they cause a shrinking of s and $p_{1/2}$ electron orbitals and change the screening of the Coulomb potential by the inner-shell electrons [2]. Currently, many-body methods such as multi-configuration Dirac-Fock (MCDF), relativistic coupled cluster (RCC) and configuration interaction (CI) are employed to study these effects [3–6]. This has motivated many gas- and liquid-phase chemistry experiments, which could be performed in the region of the heaviest elements [7–9]. The first ionization potential (IP) represents the binding energy of the most weakly-bound electron of an atom. An accurate determination of the IP provides a crucial test for our understanding of the electronic structure and the

chemical properties of an element. According to the actinide concept put forward by G.T. Seaborg [10], the actinide series consists of 15 elements starting from actinium (Ac, $Z = 89$) and ending with lawrencium (Lr, $Z = 103$). To date, the IP of 12 elements in the actinide series has been determined using resonance ionization mass spectroscopy, Rydberg convergence and surface ionization techniques [11–17]. Lr is the heaviest element for which the IP has been experimentally determined using a surface ionization technique [17] with a precision of about 0.08 eV and potentially susceptible to unknown systematic effects. Laser spectroscopy offers a far greater precision, in the μeV regime, but its application to the heaviest elements is hampered by the absence of known atomic transitions and the need for element synthesis from nuclear fusion reactions utilizing large accelerator facilities.

Recently, we reported the development of a technique sensitive enough for laser spectroscopic studies of nobelium ($Z = 102$) on an atom-at-a-time scale [18]. While this marked a first foray of optical spectroscopy into the

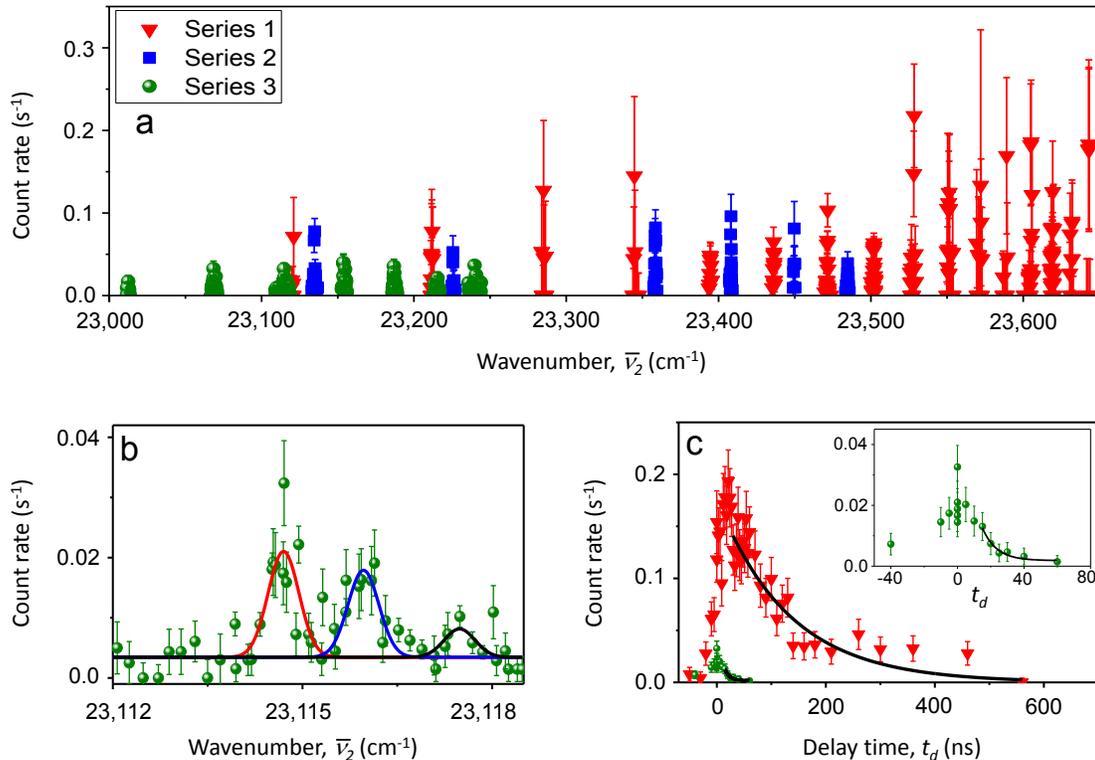


FIG. 1. (a) Scan of the second-step excitation $\bar{\nu}_2$ in ^{254}No . The first-step was fixed at $\bar{\nu}_1 = 29,961.457 \text{ cm}^{-1}$. Series 1 and 2 were measured at a argon gas pressure of 95 mbar. Series 3 was measured at a pressure of 65 mbar, to reduce the buffer gas collision induced quenching. (b) A selected Rydberg resonance proceeding from the intermediate state with Gaussian fits (solid lines) to the data. (c) Resonance ionization signal for delayed Rydberg excitation, series 1 (red points) and 3 (green points), proceeding via the intermediate states. The solid line indicates an exponential fit to the data with lifetime τ about 100 ns (series 1 and 2) and 5 ns (series 3). *Inset*, magnification of delayed ionization of series 3. The α -decay count rates are normalized to a primary beam current of 1 particle μA .

79 region of the transfermium ($Z > 100$) elements by ad-100
 80 dressing the difficulties mentioned above, an ambiguity¹⁰¹
 81 due to an inter-atomic quenching process in the nobelium¹⁰²
 82 atom led to significant uncertainties for the element's IP¹⁰³
 83 [18, 19]. Here we present the results of extended measure-¹⁰⁴
 84 ments that overcome these limitations of our previous¹⁰⁵
 85 work and which have greatly opened up the versatility of¹⁰⁶
 86 the technique. Two complementary methods have since¹⁰⁷
 87 been developed, whereby excitation to Rydberg states¹⁰⁸
 88 (prior to ionization) proceeds (i) via the direct excita-¹⁰⁹
 89 tion from an intermediate atomic state, or (ii) following¹¹⁰
 90 buffer gas collisional de-excitation to an intermediate ex-¹¹¹
 91 cited state. The first has now enabled the measurement¹¹²
 92 of the IP of nobelium with a precision three orders-of-¹¹³
 93 magnitude greater than that previously reported [18].¹¹⁴
 94 For the second, we here exploit a complementary pro-¹¹⁵
 95 cess to determine the electronic energy levels also when¹¹⁶
 96 the ground state optical transition is forbidden. ¹¹⁷

97 The experiment was performed behind the velo-¹¹⁹
 98 city filter SHIP at GSI, Darmstadt, Germany [20].¹²⁰
 99 The isotope ^{254}No (half-life $T_{1/2} = 51 \text{ s}$) was

produced in the complete-fusion evaporation reaction $^{208}\text{Pb}(^{48}\text{Ca}, 2n)^{254}\text{No}$ with a cross-section of $2 \mu\text{b}$ [21]. The lead sulfide target had an average thickness of $470 \mu\text{g}/\text{cm}^2$. The ^{48}Ca beam from the UNILAC accelerator exhibited a macro-pulse structure of 5 ms beam-on and 15 ms beam-off period. The beam intensity at a projectile energy of $4.55 \text{ A}\cdot\text{MeV}$ [22] was typically 0.7 particle μA (about 4×10^{12} particles per second). The beam was additionally gated in accordance with user-defined measurement cycles. The rate of fusion products delivered to the experiment was checked by a retractable position-sensitive 16-strip silicon detector placed at the focal plane of SHIP. The fusion products were separated from the primary beam by the velocity filter SHIP and thermalized inside an optical gas cell, filled with 95 mbar of ultra-high purity argon. A $3.5 \mu\text{m}$ thick aluminized Mylar entrance foil separated the optical cell from the high vacuum of SHIP. The thermalized fusion products that remained charged were collected on a tantalum filament of $125 \mu\text{m}$ diameter. After a collection time of 25 s [23], optimized for the half-life of ^{254}No , the incoming

beam was switched off for 5 s during which the filament was pulse heated for 300 ms to about 1350 K in order to evaporate the collected fusion products as neutral atoms. The temperature of the filament was monitored by a fast infrared pyrometer (LumaSense, IMPAC IS 6 Advanced). A two-step photoionization process was then employed to ionize the atoms. The produced ions were transported by electric fields onto a silicon detector where they were identified by their characteristic α -decay energy. The laser light was provided by two tunable dye lasers (Lambda Physik FL and LPD series) pumped by two excimer lasers with a 100 Hz repetition rate at 248 nm and 308 nm, respectively. The dye laser pulses had a pulse duration of 18 ns with a jitter of about 10 ns. The wavelengths were continuously monitored with a wavelength meter (HighFinesse-Angstrom, WS/7-UVU) that was calibrated to an internal neon lamp. A more detailed description of the experimental setup and method can be found in refs. [24–26].

A two-colour photon-excitation scheme was used to search for Rydberg states in ^{254}No . We operated one dye laser at $\bar{\nu}_1 = 29,961.457 \text{ cm}^{-1}$ initiating in a first step the $^1\text{S}_0 \rightarrow ^1\text{P}_1$ ground state transition [18] while another synchronized dye laser provided tunable light for the second excitation step, $\bar{\nu}_2$. The atoms that were successfully excited into a Rydberg state were subsequently ionized either by residual laser light, black-body radiation, or collisional processes. In total, a spectral range of the second excitation step from 23,000 to 23,650 cm^{-1} was scanned to locate 29 Rydberg states. At a buffer gas pressure of 95 mbar two different series comprising 22 Rydberg states were identified as shown in Fig. 1 a (series 1 and 2), significantly adding to those reported previously [18]. However, in this previous work it could not be unambiguously determined from which state the second excitation step originated, due to the possibility that gas induced quenching (following excitation to the $^1\text{P}_1$ intermediate state) populates close-lying long-lived states. Reducing the buffer gas pressure to about 65 mbar, helped to observe another series (series 3 in Fig. 1 a) with a substantially reduced count rate. The lowest-lying Rydberg states from this series showed resolved multiplet structures (Fig. 1 b), which can be attributed to different fine structure components. The splitting of the multiplets decreases with increasing principal quantum number.

In order to identify the state from which the second transition takes place, the α -signal at resonance was measured as a function of time delay between the two laser pulses. The first step was kept at $\bar{\nu}_1 = 29,961.457 \text{ cm}^{-1}$ populating the $^1\text{P}_1$ state and the second step was set to excite a specific Rydberg state. This measurement allows us to probe the lifetime of the intermediate state which enables the disentanglement of the different Rydberg series (see Fig. 1 c). Members of one series (3) indicate a short-lived intermediate state with a lifetime of about 5 ns in agreement with the expecta-

tions for the $^1\text{P}_1$ state. The intermediate state for the members of the other two series (1 and 2) has a longer lifetime of about 100 ns proving the involvement of an additional intermediate level populated by buffer gas induced quenching of the $^1\text{P}_1$ state.

In the data analysis of the individual resonances, we used a χ^2 -minimization routine to extract the relevant parameters. We determined the excitation energy of the Rydberg states from the centroids of single or multiple Gaussian fits to each resolved state or unresolved multiplet, respectively. The excitation energy of the Rydberg states follow a trend given by the Rydberg formula [27]

$$h\bar{\nu}_2(n) = h\bar{\nu}_{\text{lim}} - R_m/(n - \delta(n))^2, \quad (1)$$

where $h\bar{\nu}_{\text{lim}} = \text{IP} - E_{\text{interm.}}$ denotes the ionization limit for an intermediate state of energy $E_{\text{interm.}}$. h is the Planck constant, n is the principal quantum number of the valence electron and R_m is the reduced mass Rydberg constant for ^{254}No . The quantum defect $\delta(n)$ can be parameterized by the Ritz expansion [28]

$$\delta(n) = \delta_0 + \sum_{i=1} B_i/(n - \delta_0)^{2-i}, \quad (2)$$

where δ_0 and B_i are the fitting parameters. Figure 2 (upper panel) shows the position of all the observed peaks as a function of their principal quantum number (n). The assignment of n was obtained by restricting the quantum defect $\delta(n)$ between 0 and 1. **However, this choice for $\delta(n)$ does not affect the results of our analysis. However, the result of the analysis is unaffected by this choice.** The best fit according to Eq. (1) to the series associated with the Rydberg states proceeding from the $^1\text{P}_1$ state converged to a value $\bar{\nu}_{\text{lim}} = 23,482.14 \pm 0.27 \text{ cm}^{-1}$. The presence of the buffer gas induces a shift in the energy of the Rydberg states and thus in the extracted IP. Hence, after the correction arising from the pressure, which is about $-0.0060(7) \text{ cm}^{-1}/\text{mbar}$ for the homologue element ytterbium (Yb, $Z = 70$) [29], we obtain a first ionization potential for nobelium to $\text{IP} = 53,444.0 \pm 0.4 \text{ cm}^{-1}$ corresponding to $6.62621 \pm 0.00005 \text{ eV}$. Predictions of the IP of nobelium using different theoretical models [4–6, 30] are given in Table I for comparison along with the experimental value obtained in this work.

The other two series (1 and 2), converged to a mean value of $\bar{\nu}_{\text{lim}} = 23,792_{-8}^{+1} \text{ cm}^{-1}$ when taking higher-order corrections to the Ritz expansion (Eq. (2)) into account. Comparing the convergence limits of the series, it becomes clear that series 1 and 2 proceed from a state located about 310 cm^{-1} below the $^1\text{P}_1$ state. A likely assignment for this level at an energy of $29,652_{-1}^{+8} \text{ cm}^{-1}$ is the $^3\text{D}_3$ state, predicted to be 159 cm^{-1} [4] or 20 cm^{-1} [5] below the $^1\text{P}_1$ state. Other lower-lying D-states are predicted to be more than 1000 cm^{-1} below the $^1\text{P}_1$ state. The results have been summarized in Table I.

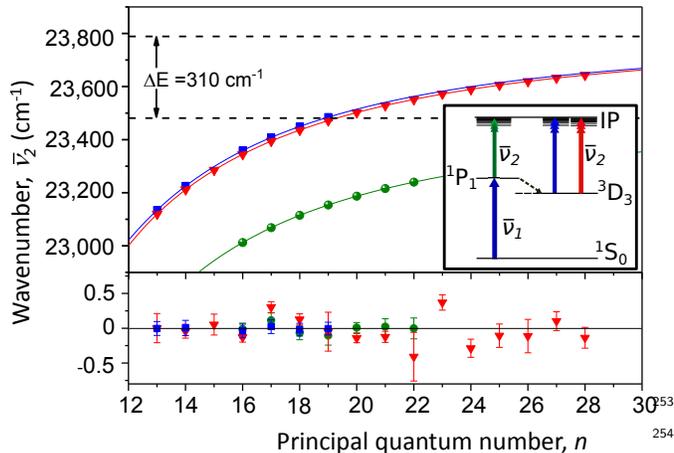


FIG. 2. Analysis of the Rydberg states. Top panel: the position of all observed Rydberg states as a function of the principal quantum number n . The Rydberg-Ritz formula, Eq. 1, was fitted to the centre position of the peaks and the main peaks of the multiplets belonging to different n . The dashed lines indicate the convergence limits of the individual series. Here, the gap between them corresponds to the energy difference between the intermediate ($1P_1$ and $3D_3$) states. *Inset*: effective level scheme for Rydberg excitation of ^{254}No . Lower panel: residuals of the fits. The uncertainty of the residuals includes the statistical uncertainty (1σ) from the fit as well as the systematic uncertainties (1σ) from the wavelength determination.

TABLE I. Experimental values of the first IP of nobelium and energy of the $3D_3$ level, compared with: IHFSCC, MCDF, CI + all orders.

Method	IP (cm $^{-1}$)	$3D_3$ (cm $^{-1}$)
Experiment (this work)	$53,444.0 \pm 0.4$	$29,652_{-1}^{+8}$
IHFSCC [4]	$53,489 \pm 800$	$29,897 \pm 800$
CI + all orders [5]	$54,390 \pm 1,100$	$30,183 \pm 1,100$
MCDF [6]	$53,701 \pm 1,100$	
Extrapolation [30]	$53,600 \pm 600$	

and the level-energy of the $3D_3$ state with high precision. In general, we found a good agreement between the predictions and our results. In particular, the intermediate Hamiltonian Fock-space coupled-cluster (IHFSCC) and configuration interaction method combined with the linearized single-double coupled-cluster (CI + all order) calculations deviate by less than 2% from the experimental value for the IP. In the case of the $3D_3$ state, the deviation is larger compared to other levels potentially due to correlation effects, underestimation of QED effects or both. Our values serve as a benchmark for the treatment of relativistic, QED and electron correlation effects in state-of-the-art calculations predicting atomic properties of the heaviest elements. Our measurements show that nobelium exhibits the highest measured first IP in the actinide series [11, 17]. In analogy to ytterbium, its lanthanide homologue, this corresponds to closed $5f$ and $7s$ atomic shells in nobelium. Experimental observations with the second, ionizing, laser excitation step delayed with respect to the first revealed that the Rydberg states are excited from two distinct intermediate atomic levels. This is in agreement with the observation of a fast quenching of the $1P_1$ state to a longer-lived state due to collisions of the excited atom with the buffer gas [19]. From the convergence of the Rydberg series the energetic position of this long-lived state was derived to be 310_{-8}^{+1} cm $^{-1}$ below the $1P_1$ state. Based on theoretical calculations and the analysis of the quantum defect, a term assignment as $3D_3$ was made for this new state, inaccessible by direct laser excitation as the optical transition from the ground state is forbidden.

This work opens the door for forthcoming precision measurements of various atomic and nuclear properties of still heavier elements using laser spectroscopic techniques, for example the precise determination of the IP for Lr, where the question about the change in the ground-state electronic configuration of Lr, predicted to be $[\text{Rn}]5f^{14}7s^27p_{1/2}$ [35], in contrast to that of its lanthanide homologue lutetium (Lu), $[\text{Xe}]4f^{14}6s^25d$ can now be addressed. Finally, the ability to optically pump the atoms has the potential to make further transitions accessible, not least for the precise extraction of nuclear properties from isotope shifts and hyperfine structure.

An assignment for each series can be obtained from the quantum defect and by comparing our results for nobelium with literature values for Yb. Figure 3 shows the measured quantum defect $\delta(n)$ in Yb and No as a function of the principal quantum number. The quantum defect values for Yb were calculated using the energy levels from references [32, 33]. Series 1 and 2 in No show a similar l -dependent quantum defect constant δ_0 of about 0.9 and 0.1 as the np and nf series in Yb (Fig. 3 left panel), respectively, and matches with the expectation [34]. The quantum defects of series 1 feature a unique trend **caused either by strong polarization effects or a strong perturbation probably due to the presence of high-lying perturbing orbitals interfering with the Rydberg series, similar to those observed for the np series in Yb [33]**. In the evaluation for extracting the IP this can be treated perturbatively by using higher order corrections in the Ritz expansion given in Eq. (2). Series 3, with $\delta_0 \approx 0.7$ is similar to the nd series in Yb. Based on these observations an assignment of np , nf and nd is proposed for series 1, 2 and 3, respectively. According to these observations, series 1 and 2 are likely to proceed via a D-state, substantiating the assignment of the intermediate state.

In conclusion the observed high-lying Rydberg states in nobelium enabled the determination of the first IP

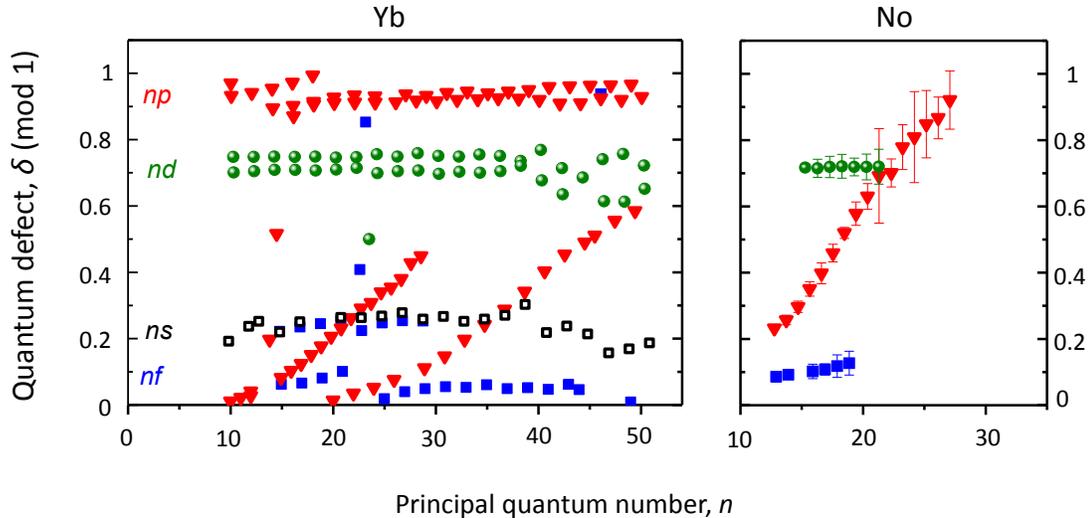


FIG. 3. Quantum defect values for Yb (left panel) and No (right panel). The quantum defects of the three Rydberg series in No and the ns (hollow squares), np (solid triangles), nd (solid spheres) and nf (solid squares) series in Yb are plotted as a function of the principal quantum number n .

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