Determination of the first ionization potential of technetium

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The first ionization potential (IP) of technetium (Tc) has been determined by evaluating Rydberg convergences toward the first ionization potential as well as toward two low-lying excited states of the singly charged Tc ion. The Rydberg states were excited and detected by applying multiphoton resonance ionization mass spectrometry (RIMS) on the long-lived isotope ^{99g}Tc using a three-color excitation scheme. The observed Rydberg convergences yield a result for the first ionization potential of Tc $V_{\mathrm{IP}}(\mathrm{Tc}) = 7.119380(32)$ eV. This precise value for $V_{\mathrm{IP}}(\mathrm{Tc})$ is somewhat lower than the so far published data of 7.23 eV or 7.28 eV, dating back to the 1950s.

I. INTRODUCTION

The first ionization potential (IP) is a fundamental quantity of high relevance; it governs the physical properties and chemical behavior of each element. Hence today only very few elements of the periodic table remain where either IP data of only very low precision or no data at all are available. These are purely radioactive or very rare elements, which cause experimental difficulties. In general, various experimental methods for IP determination exist, such as electron impact or photoexcitation via single or multistep, eventually accompanied by a static electric field [1–3]. For high-precision measurements, typically resonance ionization spectroscopy (RIS) [4,5] is used to determine the IP by observing Rydberg series and analyzing their convergences [6,7]. The corresponding spectroscopic work is tedious because narrow-bandwidth, continuous-wave lasers must be scanned across extended spectral regions. As the accurate determination of the convergence value for a series requires the observation of a sufficient number of individual levels, also high material consumption is involved. Alternatively, studies on limited sample size, that is, on rare or purely radioactive elements, apply broadband pulsed dye lasers for multistep resonance ionization on atomic vapors, accepting reduced precision [2,3,8]. Because of low ionization efficiencies of $\sim 10^{-5}$ [9], nevertheless even here macroscopic sample amounts were required. Worden *et al.*, for example, consumed ~ 2 g of ^{239}Pu, corresponding to 5×10^{21} atoms, for the accurate determination of the IP of plutonium [10]. In our work, we demonstrate how to overcome sensitivity limitations by efficiently performing resonance ionization on a thermally evaporated sample inside a hot cylindrical graphite cavity. When beams of a high-repetition-rate laser are aligned along the cavity's axis, each atom is exposed to a large average number of laser pulses before being lost by exiting the cavity. Using lasers in the kilohertz regime, ionization efficiencies around 10% have been realized by this technique [11]. In this way, the sample size can be reduced significantly. With this technique, the IP of Tc was determined from the observation of 86 Rydberg levels with a consumption of a minute amount of only 1 μg of the long-lived isotope ^{99g}Tc ($T_{1/2} = 2.1 \times 10^5$ a, $I = 9/2$), corresponding to 5×10^{15} atoms, for all measurements. Three Rydberg series were observed, one converging to the ionic ground state and two converging to different excited states of the ion. From the convergences, a value for $V_{\mathrm{IP}}(\mathrm{Tc})$ is consistently extracted, which is compared to the literature values. Because of the spectral width of the pulsed lasers and the Doppler broadening of the resonances, no attempt was made to consider the hyperfine structure of the odd mass isotope ^{99g}Tc.

II. EXPERIMENTAL SETUP

Excitation and ionization of the Tc atoms were carried out using three pulsed Ti:sapphire lasers built at the University of Mainz [12]. These were pumped by two commercial frequency doubled Nd:YAG lasers (Clark MXR-ORC1000) operated at a repetition rate of 7 kHz. Two of the Ti:sapphire lasers were equipped with a birefringent filter and an etalon for frequency selection and line width definition. They ensure high laser power and frequency stability but only limited wavelength tunability. The third laser incorporated a diffraction grating in Littrow [13] geometry to permit a continuous, mode-hop free tuning range extending from 700 to 990 nm. Temporal synchronization of pulses from the different lasers was achieved via Q-switching the resonators with a built-in Pockels cell. Spectral line width of about 5 GHz and pulse duration of 40 ns were typical specifications. With a pumping power of 15 W at 532 nm output, powers of ~ 2 W for the two standard resonators and ~ 1 W for the wide-range tunable laser in Littrow geometry were obtained. The wavelengths for the first and second excitation were monitored with a wavemeter (High Finesse WS/6), and the wavelength of the wide-range laser was measured with a second wavemeter (Atos LM-007). Both were calibrated against each other. Wavelengths in the blue and ultraviolet regimes were generated by single-pass second-harmonic generation of the fundamental Ti:sapphire light in beta barium borate (BBO, β-BaB$_2$O$_4$) and lithium triborate (LBO, LiB$_3$O$_5$) nonlinear crystals.

The atomic beam unit together with the laser system used for these investigations is sketched in Fig. 1. It contained a
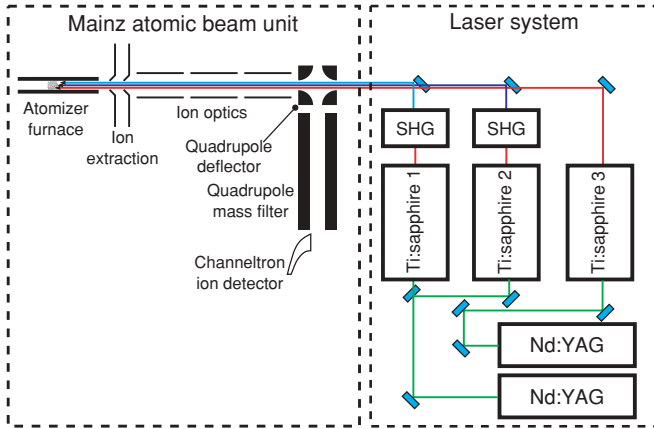
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FIG. 1. (Color online) Sketch of the setup for laser spectroscopy of Rydberg levels, including vacuum chamber and laser system.

FIG. 2. (Color online) Excitation schemes used for RIS on Tc.

graphite furnace with 2.2-mm inner diameter and a length of 50 mm, which could be resistively heated up to a maximum temperature of approximately 2800 K. Ions generated inside the oven cavity by laser ionization were accelerated to moderate energies of about 100 eV, mass separated in a commercial quadrupole mass filter for background suppression, and detected with an off-axis single-channel electron multiplier. ^{99g}Tc samples were prepared by evaporating a small volume of Tc nitrate solution on a 5×5 mm^2 piece of titanium foil. After insertion into the graphite furnace, the sample was steadily volatilized at temperatures of about 1900 K. Tc atoms were excited stepwise from the atomic ground state toward the IP by the the light from the Ti:sapphire lasers. While Rydberg levels above the first IP undergo autoionization, atoms excited to lower lying Rydberg levels were ionized either by the blackbody radiation from the hot cavity, by absorption of another photon from one of the lasers, by collisions with other atoms, or by interactions with the furnace surface. A disentaglement of these processes is cumbersome and has not been attempted.

III. RESULTS

Resonance ionization of Tc has been demonstrated earlier by Downey *et al.* [14] for preparation of Tc ultratrace isotope determination, with the goal of studying the Earth's exposure to ^{8}Be solar neutrinos. Different atomic levels in the range around 40 000 cm^{-1} excitation energy were used in this study, but to our knowledge, no Rydberg levels in Tc have been observed or localized so far. The three color excitation schemes used in the present work for investigation of Rydberg series are shown in Fig. 2, including A-factors, if known. The first excitation from the $4d^5 5s^2$ $^6S_{5/2}$ ground state into the $4d^5 5s5p$ $^6P^{\circ}_{7/2}$ level at 23 265.33 cm^{-1} was induced by frequency-doubled Ti:sapphire laser light at a wavelength of 429.82 nm [15]. Subsequently, the $4d^5 5s5d$ $^6D_{9/2}$ level at 44 919.07 cm^{-1} was populated in the second step with light from the second frequency-doubled Ti:sapphire laser at 461.81 nm [16]. Keeping the wavelengths of the two lower step lasers fixed in resonance, scans of Rydberg levels in the spectral region around the first ionization potential were
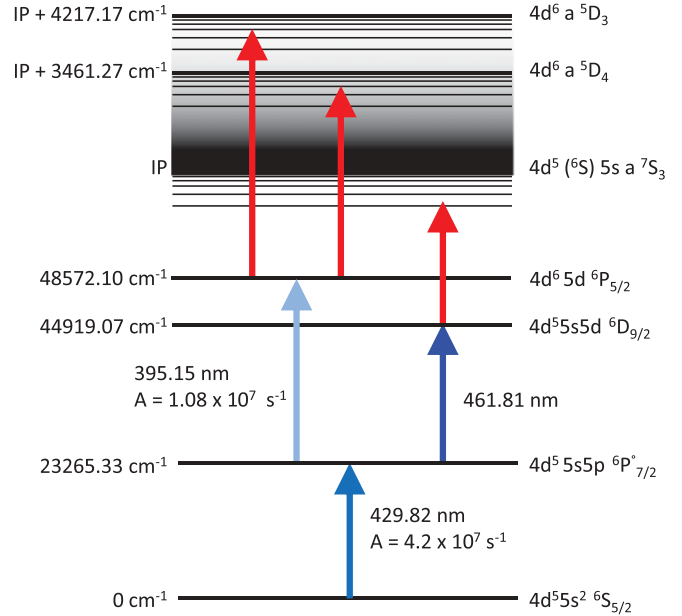
carried out using the wide-range tunable laser. In order to similarly access higher lying Rydberg levels above the first IP converging to low-lying excited states of the singly charged Tc ion, light at a wavelength of 395.15 nm was used to populate the $4d^6 5d$ $^6P_{5/2}$ level at 48 572.10 cm^{-1} [15] in the second excitation step.

By continuously tuning the wavelength of the third step laser from 837 to 900 nm, 36 members of a Rydberg series converging toward the first ionization potential were observed together with a few extra levels belonging to other configurations, so-called interlopers. The corresponding experimental data are shown in Fig. 3(a), giving the variation of the ion signal as function of the excitation energy. Figures 3(b) and 3(c) exhibit a similar scan across members of two further Rydberg series located above the first ionization potential. These converge toward the first and second excited states of the singly charged Tc ion. Therein, 34 and 16 members, respectively, have been located during a scan of the third step laser wavelength from 740 to 840 nm. Each observed resonance was fitted individually, its belonging to one of the Rydberg series was verified, and finally, the overall excitation energy of each Rydberg level was determined precisely. The symmetrical resonance shapes observed were well reproduced by Gaussian profiles with a typical line width of 0.8 cm^{-1}. This value represents the dominance of laser and Doppler contributions over the natural line profile. It additionally prevents any predictions about the hyperfine structure, which is well covered within the peak. Overall excitation energies were determined from the energetic position of the line centers by adding the precisely known energy of the individual second excited state taken from literature. All measurements were carried out in duplicate, giving full agreement and reducing the statistical variance of the measured IP values.

Because of very limited knowledge of the spectrum of Tc in the literature, the configurations of the three individual Rydberg series could not be assigned unambiguously. Nevertheless, the IP can be extracted even without a
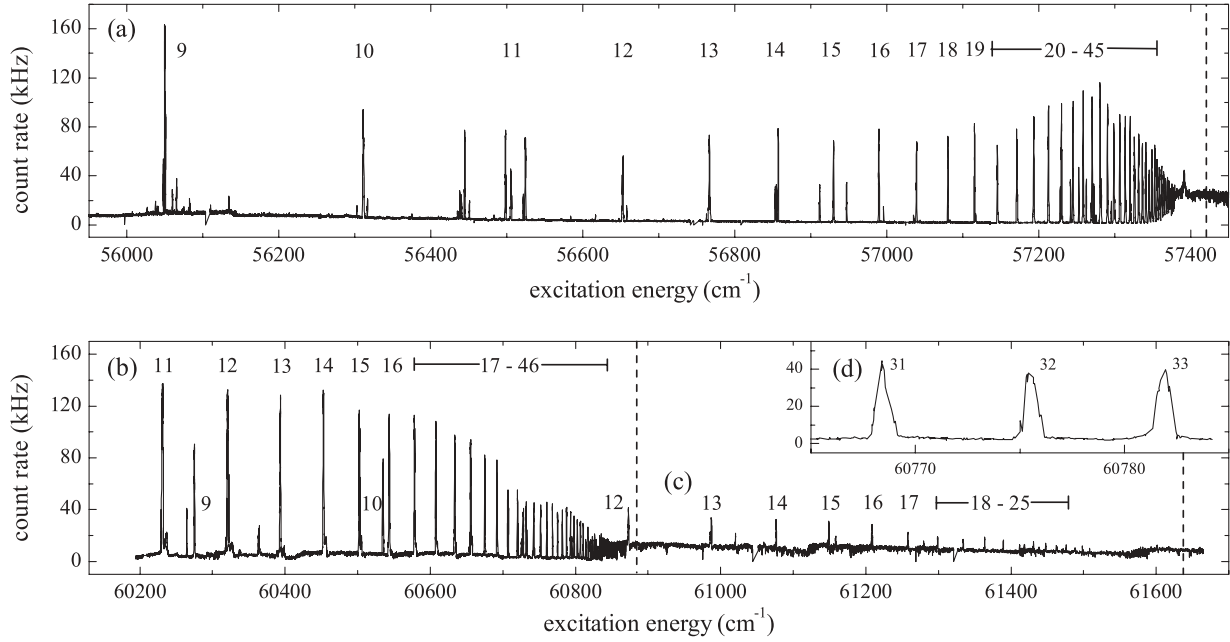
FIG. 3. Rydberg series in neutral Tc converging toward (a) the first ionization potential as well as toward (b) the first and (c) second excited states of the singly charged Tc ion. The dashed lines indicate the limits of each Rydberg series. (d) The inlay shows three resonance shapes from series (b) in detail.

configuration assignment with high precision from the individual peak positions. The Rydberg-Ritz formula

$$E_n = E_{\text{IP}} - \frac{R_M}{[n - \delta(n)]^2} \qquad (1)$$

describes the position of the levels, with R_M being the reduced-mass Rydberg constant given by

$$R_M = \frac{M}{m + M} R_\infty \qquad (2)$$

and $\delta(n)$ being the quantum defect. M and m are the nuclear and the electron mass, respectively. The quantum defect $\delta(n)$ is approximated with sufficient precision by using the well-established Ritz expansion in second order in $1/(n - A)$ [17–19]:

$$\delta(n) = A + \frac{B}{(n - A)^2}, \qquad (3)$$

where A is a constant offset and B is the J-dependent slope in the form factor of an inverse parabola. With small B-factors around $B \approx \pm 0.2$ and errors of similar size, an analysis of the development of $\delta(n)$ as a function of n does not give any further conclusive hints for configuration identification. Note that even n can only be assigned explicitly with the help of additional information such as the definite knowledge of the position of the series head from the literature. Without this, the assigned n can differ from the real n by an integer, but fortunately, this ambiguity in n does not affect the value or precision of the extracted ionization potential. Consideration of a possible Stark effect from the acceleration field would add a correction term [20],

$$E_{\text{Field}} = c_S [n - \delta(n)]^7, \qquad (4)$$

to the ionization potential. As expected from earlier measurements, it was verified in the present analysis that this term is by far smaller than the experimental uncertainties. A sizable Stark shift contribution has thus been excluded, reducing the number of open parameters in the fits. This setting is also fully supported by time structure measurements on the ion beam,
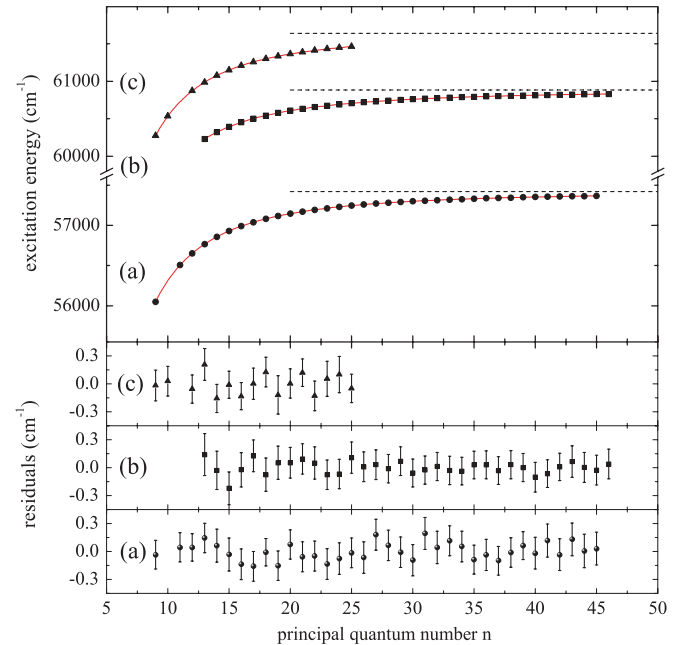

FIG. 4. (Color online) Measured Rydberg level positions and Rydberg-Ritz fits together with residuals. Convergence to (a) $4d^5$ (^6S) $5s$ a $^7S_3$ ground state, to (b) the $4d^6$ a $^5D_4$ state, and (c) the $4d^6$ a $^5D_3$ state of the ion; convergence limits are indicated by the dashed lines.
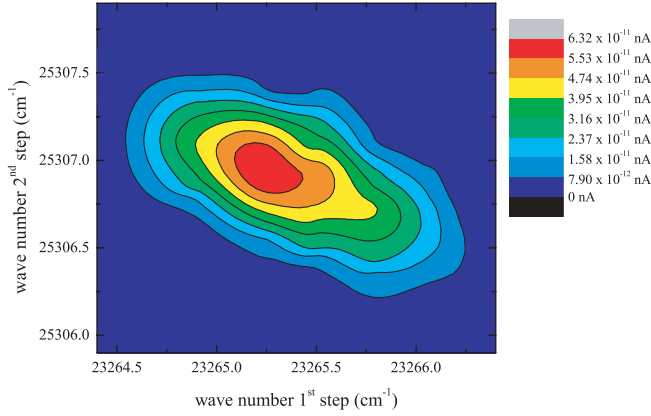
FIG. 5. (Color online) Two-dimensional laser scan of the first-step (429.82 nm) and the second-step (395.15 nm) excitation in Tc.

TABLE I. Convergence limits and ionization potentials V_{IP} of Tc derived from the individual fits. The errors given comprise different systematic and statistical contributions.

Energy of excited level (cm^{-1}) [22]	Limit (cm^{-1})	V_{IP}(Tc) (cm^{-1})
0	57 421.39(67)	57 421.39(67)
0	57 421.61(47)	57 421.61(47)
3461.27	60 882.98(48)	57 421.71(48)
3461.27	60 882.77(47)	57 421.50(47)
4217.17	61 639.23(51)	57 422.06(51)
4217.17	61 638.91(50)	57 421.74(50)

which confirmed that the majority of the atoms are ionized inside the hot cavity [21]. The field distribution in this narrow cavity is well known and amounts to less than 1 V/cm even for extraction potentials of 20 kV [11], leading to a Stark contribution in the megahertz range for levels with principal quantum numbers well below $n \approx 100$.

Figure 4 shows the energies of all observed members of the three Rydberg series together with the fit from the Rydberg-Ritz formula and the resulting convergence limits. Residuals are given at the bottom of the figures, including error bars.

In all cases, residuals do not exceed 0.2 cm^{-1} and scatter statistically, which confirms the precision of the wavelength measurement and the absence of any substantial contributions from configuration interactions with one of the interlopers in the considered levels. In the Rydberg series [Fig. 4(a)], the level with $n = 10$, and in the series [Fig. 4(c)], the level with $n = 11$ were neglected because of interferences to neighboring resonances, resulting in displacements and significantly higher residuals. The size of the error bars includes systematic uncertainties from the wavelength determination as well as errors resulting from the fit routine. They confirm the quoted precision of the data.

To precisely determine the size of the errors, Fig. 5 shows a two-dimensional laser scan of the first and second excitation steps, which prepared the Rydberg scans toward the two excited states of the Tc ion. This measurement served to particularly estimate the systematic errors on the IP values, which could result from the unresolved hyperfine structures in each individual excitation step and possible deviations of the sum of the two laser frequencies from the tabulated level energy of the line center. As the two-dimensional shape is almost perfectly symmetrical and a 20% decrease in the ion signal would have been clearly noticed during a measurement, a statistical total uncertainty of well below 0.35 cm^{-1} in

the reproduction of the tabulated energy of the second excited level by two-step laser excitation can be extracted. The additional systematic imprecision of the third-step laser frequency measurement amounts to 0.1 cm^{-1}. In addition to these possible deviations, overall errors include also a small statistical error from the Rydberg-Ritz fit to the data points. The fit results for the convergence limits of the Rydberg resonances are summarized in Table I, including overall errors. The IP values given there are derived from the individually measured limits by subtracting the precisely known energy values of the ionic excited levels of 3461.27 cm^{-1} and 4217.17 cm^{-1} [22], respectively. As errors of individual IP values do not differ significantly and the dominant fraction of the errors is statistical, that is, independent for each measurement, the final result for the IP of Tc almost perfectly matches the weighted average of the six individual measurements. This conclusive IP value was determined to be V_{IP}(Tc) = 57 421.68(26) cm^{-1}, corresponding to 7.119380(32) eV.

This value for V_{IP}(Tc) is by far more precise and, in addition, somewhat lower by about 2% than both so far published data of 7.23 eV and 7.28 eV. The first value, quoted by Finkelnburg and Humbach [23], was achieved by Catalan and Rico [24] in 1952 by interpolation techniques from known IP data of neighboring elements. The second value, adopted by Moore [22], was determined by Bozman from just two members of the $4d^6$ (a ^5D) ns $^{6,4}D$ series ($n = 5,6$) taken from [25] using a Rydberg-Ritz formula. Thus a deviation of at least the observed size was expected in a precise redetermination of this early data. Nevertheless, already the rough agreement of both values rather well confirms the adequateness of the historical, semiempirical approaches as well as the expertise of the early theorists and spectrocopists and their skill in using then available techniques.

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