PHYSICAL REVIEW A **90**, 010701(R) (2014)

# Double-$K$-vacancy states in electron-impact single ionization of metastable two-electron $N^{5+}(1s2s\,^3S_1)$ ions

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(Received 14 May 2014; published 9 July 2014)

The role of hollow states intermediately produced in electron-impact ionization of metastable He-like $N^{5+}(1s2s\,^3S_1)$ ions has been investigated in detail. A crossed-beam setup and suitable experimental techniques were employed for the measurement of accurate absolute cross sections and precise energy-scan data. Fine structures arising from $K$-shell excitations and associated resonances have been observed for this two-electron ion with less than ±0.5 eV uncertainty on the energy scale. Fine details, such as interference of the reaction pathways of direct ionization and excitation with capture of the incident electron followed by double-Auger decay, could be revealed. *Ab initio* calculations based on the convergent close coupling (CCC) approach are in good agreement with the experiment.

DOI: 10.1103/PhysRevA.90.010701 PACS number(s): 34.80.Dp, 31.15.ac, 31.15.vj, 52.20.Fs

Studying the properties and behavior of few-electron atoms and molecules is particularly interesting, since these systems can be expected to provide the best potential for understanding all details of their atomic structure and of their reactions in atomic collisions. Theoretical predictions for simple atomic systems, such as hydrogen, promise the highest possible accuracy [1] and best possible agreement with ultimate-precision experiments [2]. Next in simplicity to the extremely well-studied hydrogen atom is helium which—as the simplest many-electron atom—has also received utmost attention in both theory and experiment [3]. The three-body nature of the neutral helium atom introduces a level of complexity that has challenged fundamental theoretical concepts since the beginnings of quantum mechanics. A new twist in the endeavor to understand the fundamental complexity of a seemingly simple two-electron atom was introduced by the discovery of strong electron-electron correlation effects in doubly excited resonant states of helium in a seminal experiment by Madden and Codling [4]. The archetypical three-body system of two excited electrons in a helium atom and its physical stability has been an object of extensive research ever since ([5–7], and references therein, to name just a few).

A whole new dimension of the two-electron problem is opened when going from neutral helium atoms to heliumlike ions such as $H^-$ [8], $Li^+$ [9,10] or even $U^{90+}$ [11]. The relative strength of the electron-electron versus the electron-nucleus interaction can now be tuned by the choice of the atomic number in the He-like iso-electronic sequence and new fundamental effects originating from the increasing nuclear charge enter the stage [12].

Using helium atoms in experiments as targets for incident photons or electrons is relatively straightforward. Target pressures in the Madden and Codling experiments were up to about 30 Pa, corresponding to a density of $10^{16}$ helium atoms per $cm^3$. Correspondingly, high-precision experimental results can be and have been obtained for the quintessential doubly excited states of the helium atom (see, for example, [13]). Switching from neutral helium to beams of heliumlike ions dramatically reduces the accessible target densities—by at least 10 orders of magnitude. Thus measurements on two-electron ionic systems require extreme experimental efforts. At the same time, working with ions offers substantial advantages over gaseous targets. An ion beam can be highly purified by mass analysis and, with sufficient experimental care, the determination of the "target thickness" provided by an ion beam is superior to any other technique due to the efficient detectability of energetic ions. Moreover, the kinematics in colliding electron and ion beams favors complete collection of all product ions after the interaction.

In spite of the relative simplicity of two-electron atoms and the progress in describing their energy levels and decay probabilities, the understanding of fundamental collision processes of such systems still challenges the most involved theoretical concepts for the most fundamental multielectron phenomena. While for helium atoms in the ground state the experimental results of electron and photon scattering processes are usually described fairly well by state-of-the-art theoretical calculations [14], disturbing discrepancy is found when comparing theory with the only experiment available in the literature in which the total electron-impact single-ionization cross section of metastable $He(1s2s\,^3S_1)$ was measured [15]. While the results of that experiment agreed with older Born-type calculations, modern theoretical approaches [16–18] consistently find cross sections that are about a factor of 2 below the experimental data. This discrepancy must be clarified. New experiments of a similar nature are urgently needed. For avoiding normalization problems in such experiments, clear separation of the cross-section contributions from $1s^2\,^1S$, $1s2s\,^1S$ and $1s2s\,^3S$ parent levels is desirable. Given their electron energy spread of about 3 eV and limited statistics, Dixon *et al.* [15] could neither resolve the ionization thresholds of the two metastable levels in their cross-section data nor identify the onset of He ground-state ionization.

Along the helium isoelectronic sequence, level-energy separations increase with charge state $q$. With fixed energy resolution, details in the ionization cross sections can be resolved the better the higher $q$, provided the signal count

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rate is sufficiently high to facilitate good statistical precision. With this in mind, $N^{5+}$ ions were chosen for the present study addressing electron-impact single ionization of metastable He-like $N^{5+}(1s2s\,^3S_1)$. The triplet and singlet terms of the $1s2s$ configuration are both long lived with decay constants 256.1 $s^{-1}$ [19] and $\approx 9.5 \times 10^5$ $s^{-1}$ [20,21], respectively. The experimental data clearly show that the amount of metastable $^1S$ ions was negligible in the present measurements. Thus the parent ion beam provided a distinct component of $N^{5+}(1s2s\,^3S_1)$ ions transporting an excitation energy of as much as 419.797 eV [22] per ion into the electron-ion collision region.

Electron-impact single ionization of He-like $N^{5+}$ is predominantly associated with one-step (direct) removal of one of the two bound target electrons. Multistep processes [23] contributing to the net production of $N^{6+}$ ions involve the population of an intermediate hollow state with two $K$-shell vacancies and subsequent decay by electron emission. The excitation can be direct, or it can proceed via electron-capture resonances. In the latter case, the intermediate hollow Li-like $N^{4+}$ ion has to emit two electrons in order to finally appear in the experimentally observed net-single-ionization channel. Such indirect ionization processes starting from a ground-state He-like ion involve two-electron excitations from the $K$-shell. In contrast, the metastable He-like ion already carries a $K$ vacancy into the collision and therefore offers the simplest atomic structure starting from which a one-electron inner-shell excitation can finally result in net single ionization. Experimental identification of double-$K$-vacancy states populated during electron-impact ionization of two-electron ions requires high-sensitivity low-background interacting-beams techniques combined with high energy resolution and extremely good counting statistics. Quantifying the associated ionization contributions with good absolute accuracy additionally requires very good control of all experimental parameters. Theoretical treatment of the ionization of two-electron ions, including the indirect ionization mechanisms which proceed via hollow-state formation, calls for a unified approach beyond independent-processes, isolated-resonances approximations.

The crossed-beam experimental setup and the procedures applied are similar to what has been described previously in connection with electron-impact ionization measurements on $Li^+$ [10] and $W^{17+}$ [24]. In short, the $N^{5+}$ ions were produced from $N_2$ gas in an electron-cyclotron-resonance (ECR) ion source. The cocktail of different ion species extracted from the source was accelerated with 12 kV and mass-over-charge analyzed by a dipole magnet. A cleanly resolved beam of $N^{5+}$ ions was selected and passed through a spherical electrostatic deflector which served for final charge-state cleaning of the parent ion beam. The ion beam was crossed by an intense electron beam [25] which could be operated in "absolute mode" [26] or in "energy-scan mode" [9,27]. A second dipole magnet identical to the mass-over-charge analyzer was used to separate $N^{6+}$ product ions from the $N^{5+}$ parent ion beam. The parent ions were collected in a Faraday cup, while the products were counted by a single-particle detector after passage of a further electrostatic spherical out-of-plain deflector employed to minimize detector background from stray ions, electrons, or photons.

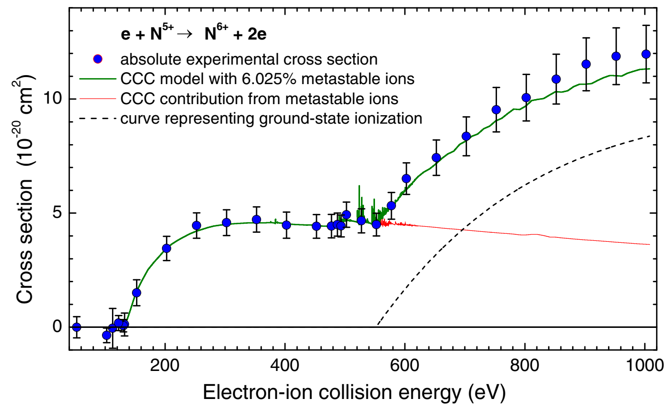


FIG. 1. (Color online) Cross section for electron-impact ionization of $N^{5+}$ ions. The full circles show the results of absolute measurements together with their total error bars. The data were obtained with an ion beam containing both metastable (ms) $N^{5+}(1s2s\,^3S_1)$ and ground-state (gs) $N^{5+}(1s^2\,^1S_0)$ ions. The solid (olive) line is the result of the present CCC calculation, assuming a fraction of 6.025% ms ions in the parent beam. The cross section for the ms fraction is the thin solid (red) line. The smooth dashed line represents the gs ionization contribution, which is subtracted from the experimental data to obtain the ms cross section.

With an ion energy of 60 keV, the flight time from the source to the interaction region was little over 4 $\mu$s, i.e., approximately four lifetimes of the $^1S$ metastable $N^{5+}$ ions, leaving no more than about 2% of the initial population generated in the ion source. Assuming statistical population of the $1s2s$ terms, one has to expect a $6\times10^{-3}$ fraction of $N^{5+}(1s2s\,^1S_0)$ relative to $N^{5+}(1s2s\,^3S_1)$ ions. Using the previously applied techniques [10,24], absolute cross sections for single ionization of $N^{5+}$ were measured in the energy range 50–1000 eV.

The present measurements were accompanied by theoretical calculations using the convergent close coupling (CCC) approach [28]. A particular effort had to be made to provide details of the cross section matching the quality of the experiment. Up to 712 states were included, which arose from up to 30-$\ell$ one-electron $N^{6+}$ orbitals for $\ell \leqslant 4$. Allowance was made for core excitation of $n \leqslant 4$ ionic states. The results of experiment and theory are shown in Fig. 1. For the CCC calculations, time-averaged fractions $a = 0.060\,25$ of $N^{5+}(1s2s\,^3S_1)$ and $(1-a) = 0.939\,75$ of $N^{5+}(1s^2\,^1S_0)$ ions in the parent ion beam were assumed. Theory agrees with the experiment well within the energy-dependent experimental uncertainty.

Employing the "energy-scan mode" [10], relative cross-section measurements were carried out with energy steps of about 200 meV. Collimated ion beams with up to 2 $\mu$A were used. Associated background count rates resulting from ionizing collisions of $N^{5+}$ ions with residual-gas molecules were typically 2 kHz. Signal count rates varied with the energy-dependent electron current (and cross section), reaching a maximum of 16 kHz at 1 keV electron energy. Approximately 1000 h of pure data taking time, distributed over about 4500 energy channels with preference to regions of specific interest, were consumed to reach statistical uncertainties as low as 0.06% in the energy range just below 400 eV. The electron

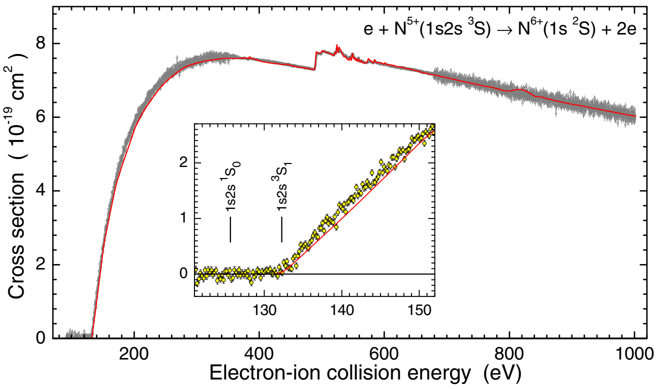


FIG. 2. (Color online) Cross section for electron-impact ionization of metastable $N^{5+}(1s2s\,^3S_1)$ ions. The data points with statistical error bars are derived from the present experiment. The solid (red) line is the result of the present CCC calculation convoluted with a Gaussian of 1.7 eV width. The inset shows the thresholds (vertical bars) of the metastable terms in comparison with the present data.

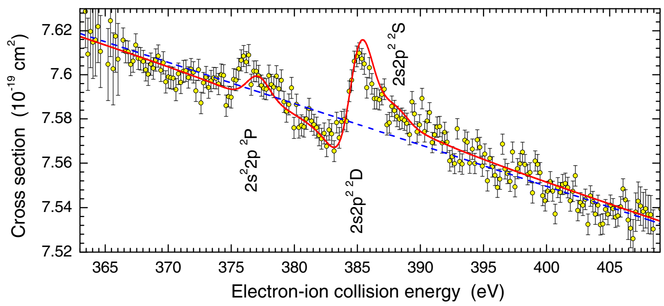


FIG. 3. (Color online) Detail of the cross section for electron-impact ionization of metastable $N^{5+}(1s2s\,^3S_1)$ ions in the energy range of READI resonances. The solid (red) line shows excursions predicted by the CCC calculation from direct single (knock-off) ionization, which is represented by the dashed (blue) line.

acceleration voltage was measured during the scans with a calibrated precision voltmeter. As in previous experiments [10], the electron energy scale was shifted down by 0.9 eV to correct for contact potentials in the wiring of the electron gun. The scan data were normalized to the measured absolute cross sections and then the apparent ground-state ionization cross section, represented by a suitably adjusted smooth curve (see Fig. 1), was subtracted to obtain the pure contribution of the metastable-ion-beam fraction $a$. Since $a = 0.060\,25$ gave the best agreement with the CCC calculation, this number was used to infer the electron-impact single-ionization cross section for $N^{5+}(1s2s\,^3S_1)$ ions, which is shown in Fig. 2 together with the CCC result.

There is no apparent signal below the $^3S$ ionization threshold that might arise from $^1S$ metastable $N^{5+}$ parent ions, confirming the purity of the metastable-ion-beam component as expected on the basis of lifetimes. On top of the smooth direct-ionization cross section, a distinct step feature is seen at around 500 eV that is due to $K$-shell excitation with subsequent electron emission. Theory and experiment are in remarkable agreement over the whole range of the present investigation. The level of statistical scatter in the experimental data indicates where the region of interest is located and where most of the data taking was concentrated. This region is scrutinized in the subsequent two figures.

The lowest energy required to excite the $1s$ electron in $N^{5+}(1s2s\,^3S_1)$ is associated with $1s \to 2\ell$ transitions with thresholds at around 490 eV. Below that energy, $K$-shell excitation is still possible when the incident electron is captured to a bound state and binding energy becomes available to aid with the $1s \to 2\ell$ transition of the core electron. This process is known as resonant dielectronic capture [23] and, in the specific case, can populate double-$K$-vacancy (hollow) states with configurations $2s2\ell2\ell'$. If signatures of such intermediate configurations are to appear in the net single-ionization channel where $N^{6+}$ product ions are observed, the hollow $N^{4+}(2s2\ell2\ell')$ ion has to emit two electrons and the only conceivable mechanism for this is double-Auger decay, i.e., simultaneous emission of the two electrons. The whole process is known as resonant excitation auto-double ionization (READI) [23]. Figure 3 shows results for the energy region where the dominant $2s2\ell2\ell'$ READI contributions are to be expected. The READI resonance features experimentally observed in the energy range 360–410 eV cause excursions in the cross section of less than 1% of the direct ($2s$ knock-off) ionization contribution. The CCC calculations show three distinct resonance features in this range. For optimum comparison of theory and experiment, the CCC results obtained on a closely spaced energy grid were fitted assuming a direct-ionization "background" represented by a second-order polynomial and three Fano profiles. The resonance parameters (resonance energies, natural widths, resonance strengths, and Fano asymmetry parameters $q$) were extracted. The isolated resonance contributions were then convoluted with a 2-eV FWHM Gaussian, shifted in energy by +0.92 eV to match the experimental resonance position of the $2s2p^2\,^2D^e$ resonance, and added to a straight line representing the smooth experimental direct-ionization "background." The resulting shifted cross-section function is the solid line in Fig. 3. It shows quite good agreement with the experiment. Obviously, the resonance channels interfere with direct-ionization channels, giving rise to loss of collision strength at certain energies and an enhancement at others. The dominant resonance channels are indicated in the figure. Possible READI contributions with one electron in a shell with a principal quantum number higher than 2 have not been observed.

The most prominent feature in the cross section appears at around the $K$-shell excitation threshold near 490 eV. The energy range of $1s \to n\ell$ excitations is shown in Fig. 4. Principal quantum numbers $n$ can be discerned up to $n = 5$. Obviously, dielectronic capture with subsequent emission of two electrons is possible, giving rise to substantial resonance contributions to the total $K$-shell excitation cross section. It is impossible to associate the peak structures in this region with specific intermediate terms. There are too many overlapping resonances not individually resolved. Nevertheless, fine structures in the $1s \to 2\ell$ direct excitation resulting from different terms in the $2s2\ell$ configuration are resolved and individual contributions of specified terms can be quantified.

At higher energies contributions of specific configurations can be associated with step and peak features observed in

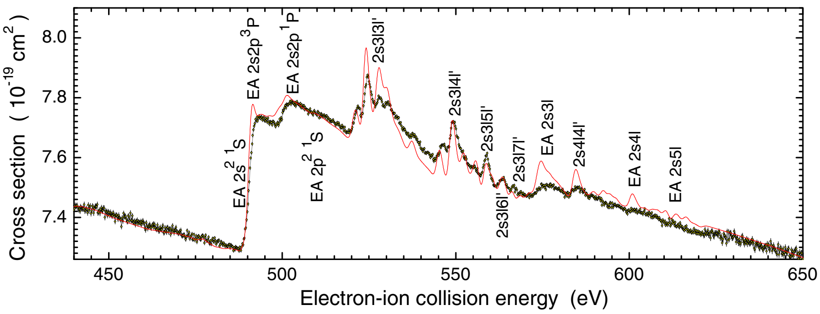


FIG. 4. (Color online) Cross section for electron-impact ionization of metastable $N^{5+}(1s2s\,^3S_1)$ ions: experiment–open circles with statistical error bars; convoluted CCC results–solid (red) line. The most prominent features are associated with levels, terms, and configurations. The abbreviation EA stands for excitation autoionization [23].

the experiment. All these fine features are related to hollow, double-$K$-vacancy states. The steps belong to two-electron intermediate (doubly excited) states and the resonances are associated with three-electron ($N^{4+}$) intermediate (triply excited) states. In the present energy region, the resonant states predominantly emit the required number (two) of electrons via sequential Auger or Coster-Kronig processes. As a result these resonances, usually termed resonant-excitation double-autoionization (REDA) [23], are considerably larger than the READI resonances seen in Fig. 3, which require correlated two-electron emission. Even at the present level of precision, the CCC calculations are in agreement with the experiment. Although not always giving perfectly the same shape of cross-section features, each kink in the experimental cross section is also found in the CCC result, at least up to electron energies of about 570 eV. Beyond that energy, the resonance features are due to $2sn\ell n'\ell'$ configurations with $n,n' \geqslant 4$. For that, there are not enough levels included in the close-coupling basis set. Including $n = 5$ is beyond the available computational capabilities.

The experimental data are of a quality as it is reached in electron-spectroscopy experiments (see, e.g., Ref. [29]). The energy scale is estimated to be correct within $\pm 0.5$ eV. The energy resolution is at least 1.7 eV at 560 eV resulting from analysis of the $2s3\ell5\ell'$ resonance group. For the energy range of the READI resonances only, which were measured for hundreds of hours distributed over more than three months, limitations in the long-term stability of the scan energies resulted in a maximum energy spread of 2 eV. This, together with the extremely low statistical uncertainties, facilitates extraction of accurate level energies even of individual triply excited states. For example, the triple-excitation energy of the $N^{4+}$ ground state inferred from the known ionization potential of $N^{4+}(1s^2 2s)$ and the $1s^2 \to 1s2s\,^3S$ excitation energy [22] plus the measured resonance position (384.63 eV, see Fig. 3) of the $2s2p^2\,^2D^e$ READI resonance is 902.31 eV, which is in excellent agreement with the theoretical data of Conneely and Lipsky, 902.28 eV [30], and Safronova and Bruch, 901.93 eV [31]. They also agree perfectly with the Auger spectroscopy data of Zouros *et al.*, $902.2 \pm 0.8$ eV [29].

In summary, the present study scrutinizes electron collisions with excited two-electron ions using state-of-the-art experimental and theoretical techniques to obtain data with unprecedented precision. While metastable-ion-beam components often plague the measurement of collision cross sections, a well-defined long-lived highly excited state of $N^{5+}$ ions has been prepared for the present measurements. Heavy-ion storage rings with cooled ion beams and ultracold electron beams, which often provide great advantages over single-pass arrangements like the present one, are not suitable for such experiments since the excited ions would have decayed before a measurement could be started. Moreover, due to high background levels in storage-ring ionization experiments, the statistical precision of the present results is superior to what can be accomplished at a storage ring.

The present detailed measurements and accompanying CCC calculations show a level of agreement of theory and experiment even in the smallest details, including the role of three-electron excited states, that provides strong confidence in the capability of this theoretical approach to obtain accurate cross sections also for the isoelectronic $He(1s2s\,^3S)$ atom, which should be revisited experimentally as a matter of urgency.

We are grateful for support by Deutsche Forschungsgemeinschaft DFG. D.F. and I.B. acknowledge the support of the Australian Research Council, and the Australian National Computing Infrastructure Facility and its Western Australian node IVEC.

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