Laser-Stimulated Recombination Spectroscopy for the Study of Long-Range Interactions in Highly Charged Rydberg Ions

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(Received 11 April 1995)

The energy shifts of high-angular-momentum Rydberg states in berylliumlike O^{4+}, due to long-range interactions of the Rydberg electron with the ionic core, are measured by laser spectroscopy, using stimulated two-step recombination of free electrons with O^{5+} ions. The comparison of the accurate experimental results with theoretical shifts from the core polarization model and from *ab initio* atomic structure calculations shows considerable disagreement, demonstrating the need for an efficient method to include configuration interaction in a long-range interaction model.

PACS numbers: 32.30.Jc, 32.10.Dk, 32.80.Rm, 34.80.Lx

Rydberg atoms and ions consisting of a few-electron core and an outer electron represent a model situation for the investigation of long-range forces caused by multipole polarization of an atomic system. In particular, the energy differences between the angular momentum sublevels nl (often referred to as electrostatic fine structure) for high principal quantum number n and high angular momentum l reflect the polarization forces between the atomic core and the distant Rydberg electron [1]. Hence, spectroscopic studies of highly excited atoms and ions provide a powerful method to investigate the polarization properties of atomic systems [2] and fundamental properties of long-range interactions, ultimately including very subtle effects such as Casimir-Polder [3] retardation forces [4].

Here we present first results on the electrostatic fine structure of a multiply charged berylliumlike Rydberg ion (O^{4+}) obtained by a novel spectroscopic method in which high-angular-momentum states of selected Rydberg levels are populated by laser-stimulated recombination of free electrons with lithiumlike ions in a heavy-ion storage ring. Transitions from specific nl sublevels to lower-lying Rydberg sublevels $n'l'$, driven by a second laser field of tunable frequency, are then detected with high efficiency. The experimental accuracy of the electrostatic fine structure, obtained in a first straightforward implementation of this technique, is 2×10^{-5} eV. This presents an improvement of about 1 order of magnitude in comparison to earlier emission-spectroscopy data on O^{4+} and other berylliumlike ions with similar nuclear charge, obtained from discharges [5] or beam-foil excitation [6,7] and provides a sensitive test of the atomic structure theory for these systems. In particular, results from multiconfiguration Dirac-Fock calculations, which gave reasonable agreement within the error of the earlier beam-foil data [7], show clear discrepancies from the present more accurate results.

Among the few-electron systems best suited for precision atomic-structure studies, berylliumlike Rydberg ions show particularly large polarization effects, as the excitation energies of the lithiumlike ($1s^2 2s$) core to the $1s^2 2p$ configurations are comparatively low. On the other hand, additional shifts of the energy levels are caused by the relatively strong configuration mixing between the two interlacing Rydberg series converging to the $1s^2 2s$ and $1s^2 2p$ core levels. Earlier experiments on berylliumlike Rydberg ions [6,7] have already revealed significant deviations from predictions of the polarization model [2,8,9]. In fact, because of the low $2s$-$2p$ excitation energy, nonadiabatic effects in core polarization are expected to become particularly important [10]. Therefore the accurate l splittings measured here can help develop a better understanding of nonadiabatic long-range forces in few-electron systems, in particular, as the spectroscopic method can readily be extended to berylliumlike Rydberg ions of other nuclear charge.

The experimental method uses an arrangement and a general procedure similar to our earlier studies of laser-stimulated electron-ion recombination [11,12]. A fast ion beam, a velocity-matched electron beam, and beams from high-intensity pulsed lasers are overlapped with each other colinearly on a length of 1.5 m inside the heavy-ion storage ring TSR of the Max-Planck-Institut für Kernphysik in Heidelberg. The recombined ions are separated from the ion beam circulating in the storage ring (circumference 55.4 m) by one of the dipole magnets and counted on a detector. During the pulses from one of the lasers, stimulated transitions of free electrons into Rydberg levels nl with a specific principal quantum number n and a wide range of angular momenta l yield a large enhancement of the radiative electron-ion recombination rate. For Rydberg ion spectroscopy, synchronized pulses from a second laser are used to stimulate transitions further down from a specific level nl to another discrete level $n'l'$. A resonance on this second transition leads to an *additional* enhancement of the recombination rate, which provides the spectroscopic signal. For the systems investigated, the recombined ions in the Rydberg level n typically cascade further down by spontaneous emission after a flight path of the order of 1 m or less, well before they reach the recombination

 0031-9007/95/75(5)/802(4)$06.00

detector. In this situation, the spectroscopic signal is obtained by saturating the free-bound transition, which implies that the recombination yield depends on the ratio of the effective spontaneous decay rate of the bound level to the stimulated free-bound transition rate. Since the radiative lifetime of the lower level $n'l'$ is shorter than that of the upper level nl, the effective decay rate and hence the recombination rate is increased by the second laser inducing transitions from nl to $n'l'$. A preliminary account of this technique and of first tests on transitions between Rydberg levels of the heliumlike ion C^{4+} was given earlier [13].

A slightly different scheme of laser-stimulated two-step recombination was employed recently in a similar storage-ring experiment [14] to make use of the higher laser-stimulated recombination rates, which can be obtained by free-bound transitions into states nl of particularly low binding energies. In this scheme, the role of the second laser transition was to stabilize the recombined ions in the weakly bound state nl against field ionization in the dipole magnet before reaching the detector.

To investigate Rydberg transitions in the berylliumlike ion O^{4+}, a current of up to 1 mA of O^{5+} ions with a kinetic energy of 129 MeV was stored in the TSR. In the electron cooling device of the TSR, the ions were merged [11] with a velocity-matched electron beam, guided in a longitudinal magnetic field of 41.9 mT, providing electrons at a density of 4.9×10^7 cm^{-3} essentially at rest with respect to the ions. The longitudinal electron temperature was 0.5(3) meV, and the transverse temperature, reduced by adiabatic magnetic expansion of the electron beam [15,16], amounted to 17(2) meV. These values were extracted from single-step laser-stimulated recombination measurements. Electron cooling [17] causes the stored O^{5+} beam to acquire the average velocity of the electron beam, determined from the electron acceleration voltage and appropriate space-charge corrections to be 0.130 74(7) in units of the speed of light. Relative variations of the beam velocity during the measurement were $<0.5 \times 10^{-4}$, and the relative longitudinal velocity spread of the cooled ion beam, deduced from the Schottky noise spectrum [17], was $\approx 2 \times 10^{-4}$ (FWHM). The laser system, operating at a repetition rate of 50 Hz, consisted of an excimer-laser pumped dye laser with a pulse length of 13 ns and a Q-switched Nd:YAG laser with 8 ns pulses. The two lasers were carefully synchronized, the remaining jitter being less than 2 ns. They were overlapped using a dichroic mirror and shot in antiparallel to the stored O^{5+} ions. The free-bound transitions into the upper $n = 16$ levels were driven simultaneously for all l values by the Nd:YAG laser whose wavelength (1064 nm in the laboratory frame) was Doppler shifted to the maximum of the stimulated-recombination yield, obtained for photon energies near the ionization threshold of the Rydberg level n. High laser intensities of ≈ 80 MW/cm^2 were applied, thus saturating the free-bound transition with a saturation parameter of ≈ 20 for the sublevels with $6 \leq l \leq 10$. The dye laser with an intensity of ≈ 2 MW/cm^2 and a linewidth (FWHM) of 2.5×10^{-5} eV stimulated transitions down to lower Rydberg sublevels $n'l'$ with $n' = 9, 10$. Its laboratory wavelength was calibrated by comparison with tabulated reference lines of Ne and Ar transitions. In order to reduce the single-step recombination background a second, slightly delayed pulse split off from the YAG laser was used to photoionize the ions remaining in the Rydberg level n as soon as they left the electron cooler section [13]; a reionization efficiency of 30% could be achieved. The time spectrum of the recombined O^{4+} ions detected after the laser pulses displays a flat background due to spontaneous recombination and an enhancement of the count rate due to stimulated recombination [11]. The gain factor representing this enhancement is defined as the ratio of the counts within the induced peak to the number of spontaneous counts within a time interval equal to the YAG laser pulse length. When plotted as a function of the dye laser wavelength or the corresponding photon energy the gain factor yields the experimental spectrum.

Spectra of the inter-Rydberg transitions from $n = 16$ to $n' = 9$ and 10, respectively, obtained in a total data taking time of 30 h, are presented in Fig. 1. The dye laser photon energy has been converted to the center-of-mass frame of the ions using the Doppler formula and the beam velocity given above. The peaks, riding on top of a constant background due to one-photon stimulated recombination, correspond to resonant two-photon transitions from the continuum to $n'l'$ via nl. Only transitions with $l' = l - 1$ are observed, since between high Rydberg levels the matrix elements for emission processes with $l' = l + 1$ are extremely small. The solid line is a fit to the data using a convoluted Gaussian

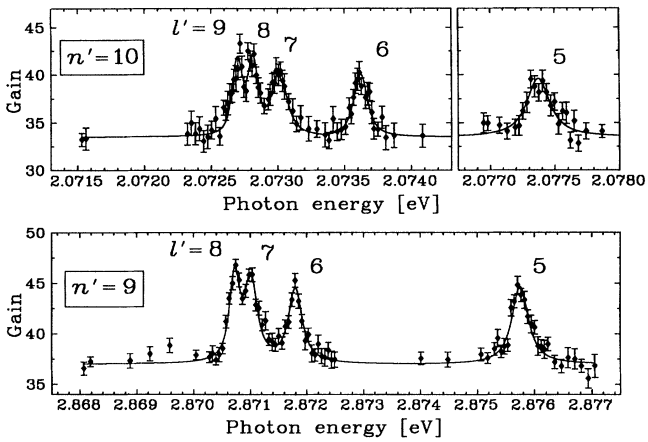

FIG. 1. Electric fine structure of inter-Rydberg transitions in O^{4+} observed by laser-stimulated two-photon recombination of O^{5+} ions into the Rydberg sublevels $n'l'$ ($n' = 9, 10$) via the intermediate levels nl ($n = 16$, $l = l' + 1$). The solid line shows a fit discussed in the text.

and Lorentzian line shape (Voigt profile) for each of the resonances. The Gaussian (Doppler) width (5.4×10^{-5} and 7.5×10^{-5} eV for the transitions 16 to 9 and 16 to 10, respectively) stems from the longitudinal ion velocity spread given above. It was fixed while the line centers and the Lorentzian widths, representing the saturation broadening of the bound-bound transitions, were fitted. As can be clearly seen in Fig. 1, the linewidth increases with decreasing l', since the oscillator strengths and hence the transition rates of both the free-bound and bound-bound transitions are higher for small angular momentum [18], leading to a larger saturation broadening; for $l' = 9, 8$ the saturation width is close to the Doppler width, whereas for $l' = 5$ it is about 4 times larger.

The resolved peaks observed for the transitions 16 to 9 and 16 to 10 are assigned by starting with $l' = n' - 1$ for the peak at the lowest photon energy. The peak intensities are in good agreement with estimates based on rate equations for the stimulated transitions, which predict amplitudes approximately independent of l'. The region between the peaks $l' = 6$ and $l' = 5$ was scanned with lower statistics and showed no further peaks. The $l' = 4$ resonances were searched for in a region where they are predicted by the polarization model but could not be found. The magnetic fine-structure splitting of the resonances lies within the experimental linewidth; the maximum splitting occurs for $n' = 9$, $l' = 5$, and is estimated to be $\approx 7 \times 10^{-5}$ eV using the GRASP atomic structure package [19]. The Zeeman splitting in the longitudinal magnetic field is $< 2 \times 10^{-5}$ eV, and the Stark shifts in the electric stray fields (space charge and motional electric fields) of < 15 V/cm are considerably smaller.

The systematic error of the beam velocity leads to an uncertainty of 1.2×10^{-4} eV of the absolute photon energy scale in the ion center-of-mass frame, whereas the relative transition energies can be given with much higher precision. The transition energies relative to the highest-l component (the line shifts Δ_{exp}) are given in Table I. They are dominated by the electrostatic fine structure splitting of the lower levels $n'l'$ but include smaller contributions from the splitting of the upper levels nl as well.

For the states with $l \geq 5$ observed in our experiment the penetration of the Rydberg electron into the ion core leads to negligible energy shifts, as can be estimated from single configuration Dirac-Fock calculations. Thus the term energies E_{nl} can be described by the hydrogenic values E_{nl}^{H} for the screened nuclear charge of $\tilde{Z} = 5$ and by corrections due to the polarization forces caused by the interaction of the Rydberg electron with the O^{5+} core. Following the standard polarization model [2], we use the parametrization

$$E_{nl} = E_{nl}^{\mathrm{H}} - \tfrac{1}{2} e^2 A \langle r_{nl}^{-4} \rangle - \tfrac{1}{2} e^2 B \langle r_{nl}^{-6} \rangle, \qquad (1)$$

TABLE I. Experimental and theoretical line shifts (units of 10^{-3} eV) among the fine-structure components of the inter-Rydberg transition from $n = 16$ to $n' = 9, 10$ in O^{4+}.

n-n'	l-l'	Δ_{exp}	Δ_{pol} [a]	Δ_{pol} [b]	Δ_{pol} [c]	Δ_{MCDF}
16-9	9-8	0.0	0.0	0.0	0.0	0.0
	8-7	0.30(2)	0.29	0.25	0.31	0.18
	7-6	1.09(2)	0.98	0.72	1.10	0.66
	6-5	5.04(3)	2.84	1.23	3.59	4.07
16-10	10-9	0.0	0.0	0.0	0.0	0.0
	9-8	0.12(2)	0.10	0.09	0.10	0.05
	8-7	0.32(2)	0.31	0.27	0.33	0.19
	7-6	0.93(2)	0.81	0.59	0.89	0.62
	6-5	4.68(3)	2.15	0.90	2.74	3.92

[a] $\alpha_d = 1.05 a_0^3$ [20], $B = 0$.
[b] $\alpha_d = 1.05 a_0^3$ [20], $B = -6.73 a_0^5$ [9].
[c] $\alpha_d = 1.05 a_0^3$ [20], $B = 3.2 a_0^5$ from fit of Eq. (1) to Δ_{exp} for $l' \geq 6$.

where the hydrogenic term energy E_{nl}^{H} includes the relativistic corrections introduced by the Dirac equation, e denotes the elementary charge, and $\langle r_{nl}^{-k} \rangle = \langle nl | r^{-k} | nl \rangle$ denote the radial expectation values for the Rydberg electron bound to a pointlike charge of $\tilde{Z}$. The two coefficients are related to the dipole polarizability α_d of the core, to its quadrupole polarizability α_q, and to the nonadiabatic correction β according to $A = \alpha_d$ and $B = \alpha_q - 6\beta$ [8,9]. All quantities can be expressed as sums over oscillator strengths and have been calculated for lithiumlike cores [9,20]; the predicted dipole polarizabilities for nuclear charges up to 9 were experimentally confirmed within 10% [6,20]. Regarding the coefficient B, however, there are striking discrepancies between calculated and experimental values. While for all berylliumlike ions B is predicted to be negative [9], the available data [5,6], although with rather large experimental errors, indicate $B > 0$. For O^{4+} Bockasten and Johansson [5] have determined $B = 2.25 a_0^5$ (a_0 being the Bohr radius) with a relative error of $\approx 50\%$, adopting a theoretical value of $\alpha_d = 1.06 a_0^3$. Curtis [9] computed values of $\alpha_q = 0.184 a_0^5$ and $\beta = 1.15 a_0^5$, leading to $B = -6.73 a_0^5$. Calculated line shifts Δ_{pol}, obtained from the term energies of Eq. (1), are compared in Table I to the measured ones. Considering only the dipole contribution, the calculated shifts are in good agreement for $l' \geq 7$ but underestimate the shifts for lower l'. Including also the theoretical B term [9], the agreement gets worse even for high l, indicating that the B term should indeed be positive rather than negative. But even allowing the coefficient B to be positive, we are not able to get a reasonable description of all the observed level shifts (see Table I).

The standard polarization model considers only the deformation of the ionic core by the field of the Rydberg electron and parametrizes it by the two polarizabilities, but it ignores the change of the dynamics of the Rydberg electron state by the interaction with the core. In a quan-

tum description, this corresponds to configuration mixing, which for berylliumlike systems couples, in particular, the singly excited Rydberg series $2snl$ with the doubly excited one $2p\tilde{n}\tilde{l}$. In order to investigate the influence of configuration mixing on the inter-Rydberg line shifts, we have performed multiconfiguration Dirac-Fock (MCDF) calculations with the GRASP atomic structure package [19], allowing for several perturbing configurations for both the upper and lower levels nl and $n'l'$. The resulting line shifts Δ_{MCDF} are given in the last column of Table I. For example, the closest perturber of the $n' = 9$, $l' = 5$ level ($2s9h$), the configuration $2p5g$, is 2.7 eV away and admixed at a level of 0.1%, which shifts the $2s9h$ energy downward by 4.5 meV. However, although similar MCDF calculations were in good agreement with earlier, less precise experimental Rydberg transition energies [7], the present measurement reveals clear discrepancies and calls for improved calculations of the electrostatic fine structure. Within the core-polarization model, the precision might be improved by a more detailed consideration of nonadiabatic effects similar to an earlier discussion performed for heavier alkaline-earth Rydberg atoms [10].

In conclusion, we have applied the technique of laser-stimulated two-photon recombination for the spectroscopy of high-angular-momentum nonpenetrating Rydberg states in O^{4+} ions. The energies of inter-Rydberg transitions could be determined with a precision of $\approx 10^{-5}$, which is about 1 order of magnitude better as achieved in earlier emission-spectroscopy data. A comparison of our data with the polarization model, parametrizing the long-range electron-ion interaction, clearly shows the need for more precise calculations. In future experiments we plan to further improve the spectral resolution by reducing the saturation broadening and to suppress the first-order Doppler width by using Doppler-free two-photon spectroscopy in counterpropagating laser beams for the bound-bound transition. The method can be readily transferred to berylliumlike ions of different nuclear charge and to other isoelectronic sequences.

We thank B. Fricke, S. Frischat, and H. A. Weidenmüller for fruitful discussions and theoretical assistance, and A. E. Livingston for providing independent MCDF results as a cross-check of our calculations. This work has been funded in part by the German Federal Minister for Education, Science, Research and Technology (BMBF) under Contract No. 06 HD 562 I (3).

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