Studies of xenon atoms in high Rydberg states*

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Thermal beams of xenon atoms in single high Rydberg states have been produced by photoexcitation of Xe($^3P_0$) metastable atoms. The highly excited states which were populated in this way were identified as $np[1/2]_1$ with $11 \leq n \leq 16$ and $nf[3/2]_1$ with $8 \leq n \leq 40$. The field ionization characteristics and radiative lifetimes of these atoms have been studied.

I. INTRODUCTION

For sufficiently large principal quantum number n, a high Rydberg atom consists of a single excited electron moving in a distant orbit in a near-Coulomb field of essentially unit charge. Such atoms are therefore expected to be near hydrogenic in character. Simple Bohr theory indicates that for $n=25$ the mean radius is approximately 500 Å and that the binding energy of the excited electron is only 20 meV. Quantum mechanical treatments[1,2] show that the radiative lifetime of this level lies between 3 and 500 μsec, depending on the orbital angular momentum l.

High Rydberg atoms, produced in electron capture collisions of fast ions during passage through a gaseous target, have been studied by several investigators. Riviere and Sweetman[3] observed the production of hydrogen atoms in states $n=9-23$, while Il'in *et al.*[4] investigated the production of helium atoms in states $n=9-17$. Bayfield and Koch[5] have recently studied mixtures of highly excited hydrogen atoms within the range $44 \leq n \leq 69$.

High Rydberg atoms may also be produced by electron impact excitation of ground-state atoms. Cermak and Herman,[6] Hotop and Niehaus,[7] Kupriyanov,[8] and Shibata *et al.*,[9] have all used this method to produce beams of high Rydberg atoms with an unknown mixture of n in the range $n=20-40$.

The main limitation of both these experimental approaches is that in neither case can a beam of atoms in a single high Rydberg state be produced. The high resolution afforded by optical excitation may, however, be utilized to produce atoms in a single state of known principal quantum number n and orbital angular momentum l.[10]

In recent experiments in this laboratory,[11-13] argon, krypton, and xenon metastable atoms, produced by electron impact excitation of ground-state atoms, were optically excited to autoionizing levels using a tunable dye laser. In the present experiment, xenon $^3P_0$ atoms have been photoexcited to high Rydberg levels which lie just below the first-ionization limit $Xe^+(^2P_{3/2})$. The production and certain properties of these highly excited atoms have been investigated as a first step toward the study of collision processes involving such species.

II. EXPERIMENTAL APPROACH

Details of the apparatus, a schematic of which is shown in Fig. 1, have been described previously,[14,15] and only the essential features are summarized here. A beam of xenon atoms, containing a small fraction of atoms in metastable $^3P_{0,2}$ states produced by electron impact, was intersected at right angles by the output beam of a pulsed dye laser which was tuned to excite transitions from the $^3P_0$ state to selected high Rydberg levels. This laser, which was pumped by a pulsed nitrogen laser, was similar to that described previously[15] except that a beam-expanding telescope was inserted into the laser cavity to reduce the linewidth to approximately 0.5 Å. The laser was operated at a pulse repetition rate of 7 pulses/sec and had a pulse power of about 50 kW and a pulsewidth of ~ 4 nsec. In the present work the laser was operated in the range $4640 \lesssim \lambda \lesssim 5100$ Å, and wavelength determinations were made using a $\frac{1}{2}$-m Jarrel-Ash spectrometer. The average laser power was measured with an Eppley thermopile.

Two techniques were used to detect the high Rydberg atoms. The first of these takes advantage of the fact that the photons in the pulse used to resonantly excite the xenon metastables were energetic enough to photoionize the resulting highly excited atoms. As a consequence, some of the high Rydberg atoms were photoionized during the remainder of the same pulse. The resulting ions were collected using a weak electric field (~ 50 V/cm) and detected using a Johnston particle multiplier. A gating technique was used to distinguish these ions from those produced by chemi-ionization of the residual gas by the xenon metastables in the beam.

The second detection technique, field ionization,[16] was used when the high Rydberg atoms lay

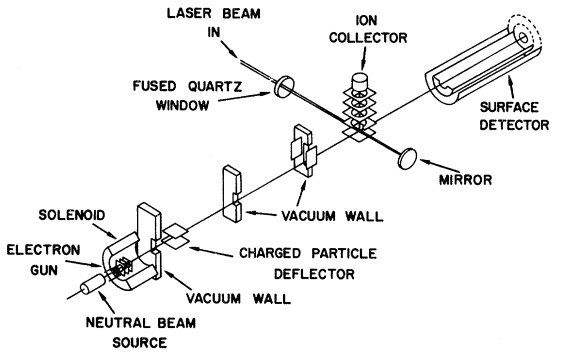

FIG. 1. Schematic diagram of the apparatus.

sufficiently close to the $Xe^+(^2P_{3/2})$ continuum. Ionization of the high Rydberg atom was then induced by the application of a strong electric field (≤ 1.5 kV/cm) across the interaction region approximately 0.5 μsec after each laser pulse. This time delay, in conjunction with suitable gating, permits the discrimination of these ions from those formed by photoionization during the laser pulse.

III. RESULTS AND DISCUSSION

A. Detection by photoionization

The data obtained using photoionization to detect the excited atoms are shown in Fig. 2. The ion count rate is normalized to unit metastable atom density and the square of the photon flux. Owing to nonreproducibilities associated with the spectrometer grating drive mechanism, and also the difficulty of precisely tuning the laser, the wavelength determinations have an uncertainty of ± 0.4 Å. The observed spectra may be interpreted with the aid of the partial term diagram shown in Fig. 3, which includes in addition to the metastable levels several members of the *nf* and *np* series. The electric-dipole transitions which result in the production of high Rydberg atoms are

$$Xe(^2P_{1/2})6s'[1/2]_0 \rightarrow Xe(^2P_{3/2})np[1/2]_1 , \quad (1)$$

$$\rightarrow Xe(^2P_{3/2})np[3/2]_1 , \quad (2)$$

$$\rightarrow Xe(^2P_{3/2})nf[3/2]_1 . \quad (3)$$

In order to identify the levels that were excited, a simple quantum-defect extrapolation from the previously tabulated[17] lower members of these series was used to obtain approximate term values for the higher members, using the relation

$$T_n = R/(n-\delta)^2 ,$$

where R is the Rydberg constant, n is the principal quantum number, and δ is the quantum defect. Values of δ were obtained from the highest previously known levels and were assumed to be independent of n for a given l. This procedure gave δ values of 0.043 for the $nf[3/2]_1$, $n>11$ series, 3.59 for the $np[1/2]_1$, $n>13$ series, and 3.52 for the $np[3/2]_1$, $n>13$ series. In Fig. 2 the calculated wavelengths are shown above the observed spectrum. It is evident that there is no ambiguity in regard to the identification of the observed $np[1/2]_1$ and $nf[3/2]_1$ levels. Transitions corresponding to excitation of $np[3/2]_1$ levels are seen to be very weak. Two very large peaks which correspond to the excitation of atoms from the $^3P_2$ metastable state to the $6p'[3/2]_1$ and $7p[1/2]_1$ levels were also observed, but have been omitted from Fig. 2 for the sake of clarity. The positions of these peaks, which are accurate-

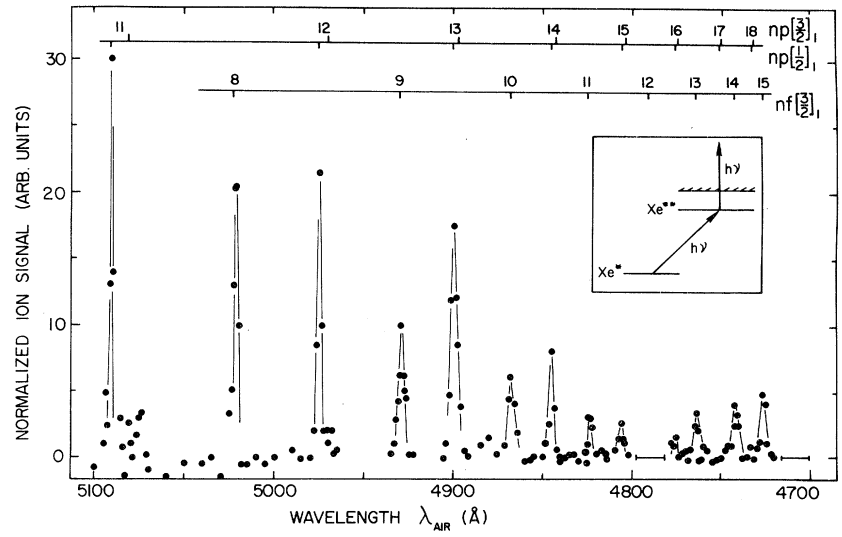

FIG. 2. Two-photon ionization of xenon $^3P_0$ metastable atoms as a function of wavelength.

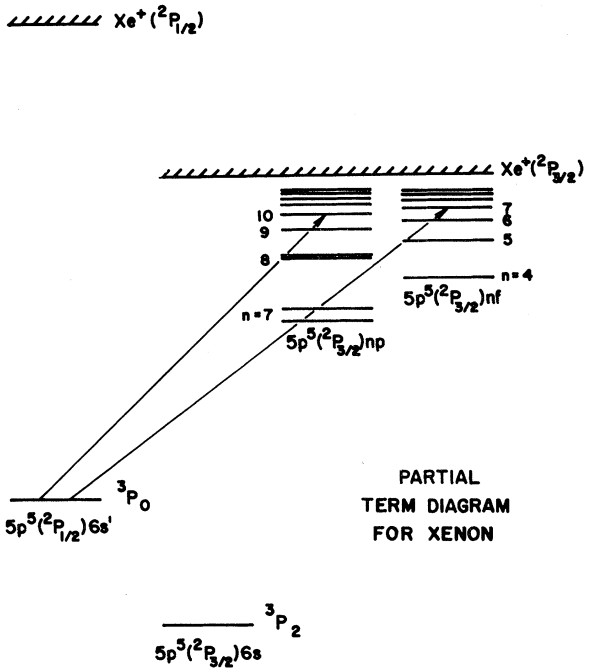

FIG. 3. Partial term diagram for xenon. Transitions of the type observed in the present experiment are indicated by arrows.

ly known,[17] were used to calibrate the spectrometer.

The spectra exhibit several interesting features. Contrary to the selection rules for jl coupling ($\Delta j = 0$; $\Delta K = 0, \pm 1$; $\Delta J = 0, \pm 1, 0 \not\to 0$), the observed transitions involve a unit change in j, the total angular momentum of the core. Thus, while jl coupling may be more appropriate than either LS or jj coupling, it is by no means entirely satisfactory. Furthermore, the $s' \to f$ transitions indicate that one or both of the levels involved would be better described by a superposition of configurations. The line intensities do not correspond with the simple empirical rule[18] for strongly favored transitions, $\Delta J = \Delta K$, which predicts that transition (2), which is only very weakly observed, should be more strongly excited than transition (1), which in fact dominates the excitation to p states. It is noteworthy that the Rydberg states observed in this work cannot be excited directly through electric-dipole transitions from the ground state.

Rare-gas spectra often exhibit strong perturbations in both intensity and position because of configuration interaction between series and levels having the same parity and J. The major perturbations of the levels of p series normally arise from interactions with the levels of the p' series. Similarly, the f series is usually perturbed most strongly by the f' series. However, in the case of xenon, where the separation of the two series limits is large, only one member of the p' series and none of the f' series lie below the lower series limit in the region of the p and f levels. Therefore, these effects would be expected to be relatively small, especially in the case of the f series. No perturbations in position are in fact observed, although a large perturbation in the intensity of the p series is observed, the np peaks becoming too weak to be seen for $n > 16$. Similar intensity perturbations have been observed previously in the absorption spectrum of argon[19] and are predicted by Fano and Cooper.[20] In the present case it seems likely that the rapid drop in intensity of the np series with increasing n is due to the presence of the $7p'[1/2, 3/2]_1$ levels which lie just above the np series limit.

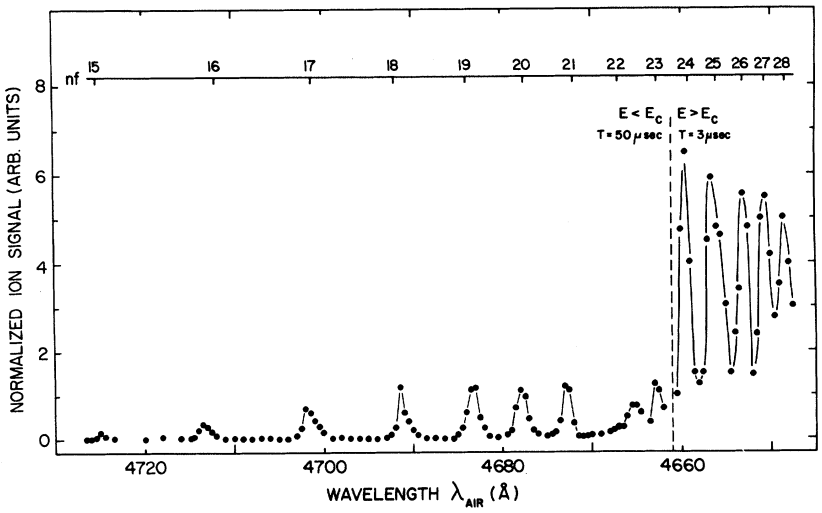

FIG. 4. The ion signal resulting from field ionization as a function of wavelength. The applied electric field (1.5 kV/cm) is insufficient to ionize efficiently high Rydberg levels with $n \leq 23$.

B. Field ionization

Field ionization was studied by applying electric fields of varying strength approximately 0.5 μsec after the termination of the laser pulse and observing the ions produced during a time interval T immediately following the application of this field. The field-ionization spectrum (Fig. 4) represents a continuation of the photoionization spectrum, and consists of f terms only, up to $n=28$. For $n>28$, individual levels could not be distinguished because of the limited laser linewidth and Stark broadening of the levels caused mainly by a small amount of field penetration at the interaction region. The absence of any strong perturbations in position means that the f levels can be numbered unambiguously.

Figure 5 shows the ion count rate, with $T=3$ μsec, observed as a function of field strength for Xe($28f$). A sharp onset followed by a plateau is observed, indicating that above a certain critical field E_c, essentially all the high Rydberg atoms are ionized in a time less than 3 μsec. With the pulsed fields currently attainable in our laboratory, atoms in states of principal quantum numbers $n \geq 24$ were detectable in this way. For states with $n<24$, only a small fraction of the excited atoms could be field-ionized and detected. It is of interest to compare the values E_c obtained in the present experiment for highly excited states of xenon with those observed in other atoms. Riviere and Sweetman[3] and Il'in *et al.*[4] have measured the fields required to field-ionize excited hydrogen and helium atoms, respectively, with an ionizing probability $W=10^{10}$ sec^{-1}. In the present experiment, $W=3.3\times10^{5}$ sec^{-1}; it is thus four or five orders of magnitude lower than in the hydrogen and helium experiments. However, according to hydrogenic theory,[16] this corresponds to a lowering of E_c by only (15–20)%, and so a comparison is of value and is shown in Fig. 6. When allowance is made for the different value of W, the present results can be seen to be in satisfactory agreement with the extrapolated values for hydrogen and helium. Il'in[21] has pointed out that for a fixed W, the experimental values of E_c fit an expression of the form $E_c=Kn^{-S}$, where K is a constant which depends on geometrical factors, and $S=4$. The present results are found to fit an expression of the form $E_c=(6.2\times10^{8})n^{-4.1}$. Thus, highly excited xenon atoms field-ionize in a near-hydrogenic

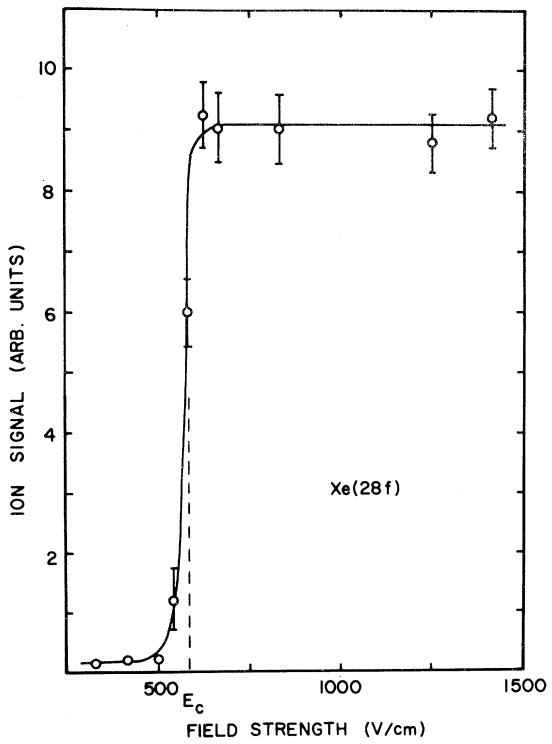

FIG. 5. Ion signal as a function of field strength for Xe($28f$), $T=3$ μsec.

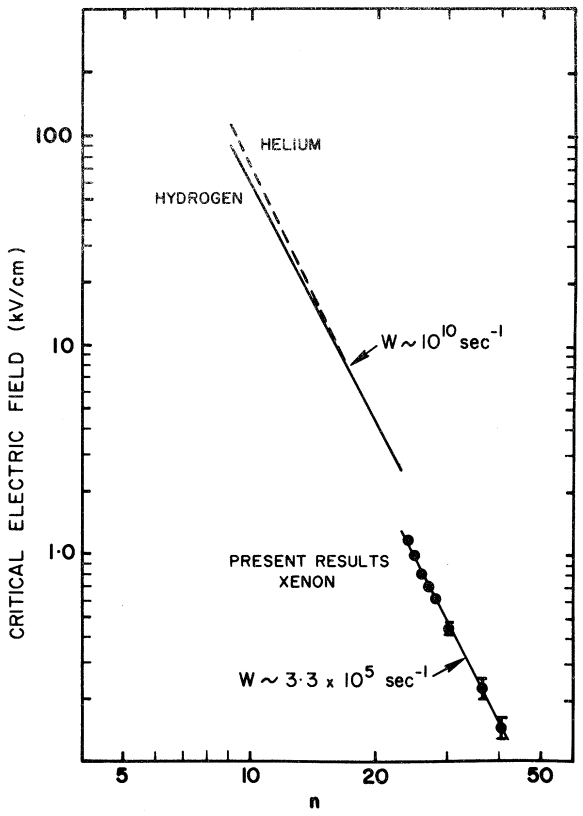

FIG. 6. Critical electric field strength E_c as a function of principal quantum number n. Experimental and theoretical results for hydrogen (Ref. 16) coincide. The experimental results for helium are from Ref. 4.

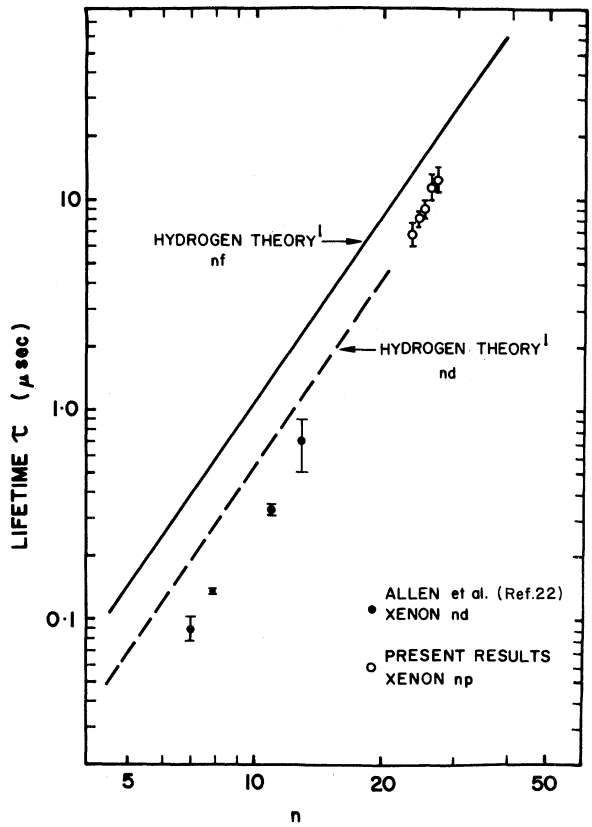

FIG. 7. Radiative lifetimes of highly excited xenon atoms.

manner, and the process can be used to detect high Rydberg atoms with essentially 100% efficiency. Furthermore, when the high Rydberg atoms have a well-defined angular momentum, as in the present experiment, the number of atoms in a given single high Rydberg state may be absolutely determined by observing the difference in the signals obtained using two electric fields, one just above and one just below the critical field for the state in question.

C. Radiative lifetimes

The main advantage in using laser excitation in lifetime measurements over the usual electron-impact method is that only the state of interest is excited, and cascade corrections are not required. To determine natural lifetimes, the number of high Rydberg atoms $N(t)$ in a given state, determined as described above, was measured as a function of the time delay t between the laser pulse and the application of the ionizing field. The natural lifetime τ was then obtained for values of $t \leq 40$ μsec, the transit time of the atom across the field of view of the multiplier, using the relation

$$N(t) = N(0)e^{-t/\tau} .$$

The measured radiative lifetimes for xenon atoms in states $24f-28f$ are shown in Fig. 7 along with the lifetimes of some highly excited d states obtained by Allen *et al.*[22] using electron-impact excitation. As might be expected, the experimentally determined values are, in both cases, near-hydrogenic. In the present experiment the lifetimes were found to be sensitive to the presence of a small residual electric field across the interaction region. For example, the lifetime of the $25f$ state increased from 8 to 24 μsec when the residual field was increased from 0 to 25 V/cm. This is presumably due to Stark-induced mixing of the substates of the n level since, according to hydrogenic theory, the lifetime of an n level averaged over all substates is substantially longer than that of an nf level. The lifetimes shown in Fig. 7 correspond to a residual electric field less than 0.1 V/cm and so should closely approximate the field-free lifetimes.

IV. CONCLUSION

It has been shown that a two-step process, electron-impact excitation to a metastable level followed by optical excitation to a higher level, can be used to produce beams of xenon atoms in a selected high Rydberg state. The field-ionization properties and radiative lifetimes of these hitherto unobserved highly excited atoms have been shown to be near-hydrogenic. It is thus possible to conduct studies of their collisional properties using atomic beam techniques. Field ionization enables essentially all the highly excited atoms ($n \geq 24$) to be ionized and subsequently detected. The production rates of these high Rydberg atoms (in the present experiment about 50 atoms/sec) can therefore be determined absolutely.

Thus it is now possible to study the collision properties of high Rydberg xenon atoms and obtain, for example, absolute cross sections for collisional ionization as a function of principal quantum number. Measurements of this type are now in progress in this laboratory.

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†On leave of absence from the Queen's University of Belfast, Belfast, Northern Ireland.

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