cross section is entirely due to the $5d \rightarrow \epsilon p$ channel which is quite small since it is just above the zero in $R_p(\epsilon)$ as seen in Fig. 1(a). The "window" is so narrow because of the rapidity of the contraction of the ϵf wave function (increase in δ_f) in the energy range around the potential barrier height. This minimum is in contrast to the relatively smooth effects of the second zero in $R_f(\epsilon)$ which gives rise to the usual Cooper minimum as shown in the inset in Fig. 2. The "window" in the cross section looks very much like autoionizing window resonances[9,10] but is really from the effect of a shape resonance.

The first minimum arises if $\delta_d(0)$ is sufficiently larger than $\delta_f(0)$ (by $\sim 2\pi$ at least). By using quantum-defect theory[11] we get these phase shifts from experimental energy-level data and we find that our calculated values are substantially correct. Thus, despite the simple Hartree-Slater potential used in the calculation, we feel that our results are at least qualitatively correct. A more exact calculation (Hartree-Fock, close-coupling, or many-body-perturbation theory) would modify the position and shape of the minimum somewhat, but would not alter the basic structure. In addition, a fine-structure effect on the ϵf wave function (the Fano effect[12]) would tend to obliterate the first minimum somewhat. It is nevertheless felt that it will be quite observable and one reason cesium was picked for calculation was that the energies involved are accessible with lasers so that the experiment is possible despite the fact that the $5d$ in Cs is not metastable as it is in Ba.

From the above discussion, it is clear that the double minima will occur over a broad range of excited atoms. We have already determined that it occurs for $5d$ from $Z = 37$ to 55 and for $6d$ over an even wider range of Z's. Work is in progress to determine the details of where and under what conditions these new minima appear.

Finally we note that this effect has been seen[13,14] in discrete photoexcitation of Ba^+. It was this that called our attention to the new minima and we gratefully thank Professor Ugo Fano and Dr. C. D. Lin for bringing it to our attention.

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[1]J. W. Cooper, Phys. Rev. Lett. 13, 762 (1964).
[2]U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 441 (1968).
[3]S. T. Manson and J. W. Cooper, Phys. Rev. 165, 126 (1968).
[4]E. J. McGuire, Phys. Rev. 170, 20 (1968).
[5]J. A. R. Samson, Advan. At. Mol. Phys. 2, 178 (1966).
[6]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963).
[7]S. T. Manson, Phys. Rev. 182, 97 (1969).
[8]A. R. P. Rao and U. Fano, Phys. Rev. 167, 7 (1968).
[9]U. Fano and J. W. Cooper, Phys. Rev. 137, A1364 (1965).
[10]R. P. Madden and K. Codling, J. Opt. Soc. Amer. 54, 268 (1964).
[11]M. J. Seaton, Proc. Phys. Soc., London 88, 801 (1966).
[12]U. Fano, Phys. Rev. 178, 131 (1969).
[13]U. Fano, private communication.
[14]C. D. Lin, private communication.

Stark Ionization of High-Lying States of Sodium*†

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By using stepwise excitation in an atomic beam, we have excited slow-moving atoms to pure high-lying quantum states at densities low enough to avoid loss by collision. The atoms were detected with high efficiency by Stark ionization. Results are presented of a study of the threshold field for ionization for s states of sodium with principal quantum number n from 26 to 37.

We report the production of highly excited sodium atoms in pure quantum states, and observations on their ionization threshold in an electric field. There has recently been a growing interest in the properties of high-lying states of atoms near the ionization limit. These states, which are essentially hydrogenic, are characterized by very long lifetimes, large polarizabilities and

Stark shifts, low binding energies ($[2n^2]^{-1}$ a.u.) and large radii (proportional to n^2 a.u.). They are so fragile and large that until recently the only data on atoms in pure high-lying quantum states have come from radioastronomical observations of the recombination lines in interstellar hydrogen.[1] Measurements on lifetimes in sodium s and d states with n up to 13 using laser excitation in a gas cell have been reported by Gallagher, Edelstein, and Hill.[2] Bayfield and Koch[3] created a beam of hydrogen with n in the range of 63 to 69 by charge exchange of a fast proton beam with xenon. Cook, West, Dunning, and Stebbings[4] have excited high-lying levels of rare gases. In our work, we have used an atomic beam to reduce collisional ionization which can limit the levels observable in a cell. By using tunable lasers, we have been able to excite selectively individual quantum states, in contrast to collisional techniques which generally excite a wide distribution of states.

Sodium atoms in an atomic beam were excited stepwise by two pulsed dye lasers[5] pumped by a common nitrogen laser. The first dye laser saturated the D_1 line (5890 Å), creating a large population in the $3^2P_{3/2}$ state, while the second (~4100 Å) caused transitions from the p state to high-lying s or d states. The lasers both had a spectral width of 1 cm^{-1}, a pulse length of 5 nsec, and a peak power of 1 kW.

We first detected atoms in high-lying levels by observing resonance fluorescence at the ~4100 Å line from the high level. A photomultiplier tube detected the light emitted at right angles to both the atomic beam and the incident lasers. We were able to observe s and d states from $n=15$ to about 30, but not higher levels because of rapidly decreasing signal strength. The intensity loss was due to two factors, each varying as n^{-3}: the decreasing transition moment, and the loss of signal which occurs when the radiative lifetime becomes longer than the time for an atom to pass out of the observation region, about 10 μsec.

For $n>23$ the excited atoms were detected by direct ionization in an applied field. In addition to avoiding the problem of signal loss due to long radiative lifetime, the method provides close to 100% detection efficiency and very low background. The laser beams intersected the atomic beam between electric field plates. A pulsed ionizing electric field was applied after laser excitation and the resulting ions were observed with a channel electron multiplier. As expected, for reasons explained below, the approximate ionization field for a state with principal quantum number n was $[16n^4]^{-1}$ a.u. (386 V/cm for $n=30$). For a typical atomic-beam density of 10^8 cm^{-3} and an interaction region of 0.02 cm^3, we observed the equivalent of approximately 10^4 ions/pulse for $n=30$.

To confirm the identity of excited levels as s or d, we used the fact that optical selection rules for stepwise two-photon processes are strongly affected by nuclear coupling in the intermediate state. The electron-nuclear hyperfine interaction mixes states of different values of m_J and m_I (where $\hbar J$ and $\hbar I$ are the electronic and nuclear angular momentum, respectively) to create a state of total angular momentum $\hbar F$. This tends to scramble together states of all possible values of m_J and m_I satisfying $m_J+m_I=m_F$. The result is that cw absorption of two photons circularly polarized in the same sense gives rise to both $s\rightarrow p\rightarrow s$ and $s\rightarrow p\rightarrow d$ transitions. In contrast, if such photons are absorbed successively in a time interval which is short compared to the hyperfine period of the intermediate state, the electron does not have sufficient time to precess about the nucleus to a new spatial orientation before it absorbs the second photon. In this situation the electric dipole selection rules for the two-step process are the same as those for an atom with no nuclear spin. For such an atom $s\rightarrow p\rightarrow d$ transitions are still allowed, but $s\rightarrow p\rightarrow s$ transitions are forbidden.

In our experiment we found, consequently, that when the lasers were circularly polarized in the same sense, the population of the s levels was a sensitive function of the delay between the pulses. When the two pulses excited the sodium in rapid succession (≤ 3 nsec delay, a time short compared to the hyperfine period in the $3P_{3/2}$ state) the transition rate to the s state was radically suppressed, whereas the rate to a d state was essentially unchanged. When the second pulse was delayed approximately 8 nsec, the s-state transition rate became far less affected by circular polarization of the lasers.

The energy levels of sodium have the form $W_n^0=[2(n-\Delta)^2]^{-1}=[2(n^*)^2]^{-1}$, where the quantum defect Δ depends on the orbital angular momentum. The high-lying levels form a slowly varying pattern shown in Fig. 1. The term spacing is $\Delta W_n^0=(n^*)^{-3}$. For $n=30$, $\Delta W_{30}^0=9.3$ cm^{-1}. The states ns and $(n-1)d$ form a pair separated by about 0.35 of the term spacing. Individual levels were resolved for $n=23$ to $n=38$. The laser frequency was determined by a Spex 14018 monochromator

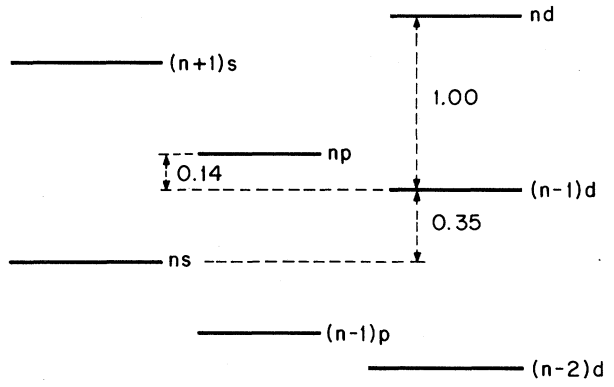

FIG. 1. Energy-level diagram showing relative positions of ns, np, and nd levels. Energy differences are in units of $\Delta W_n{}^0 = |W_n{}^0 - W_{n-1}{}^0|$.

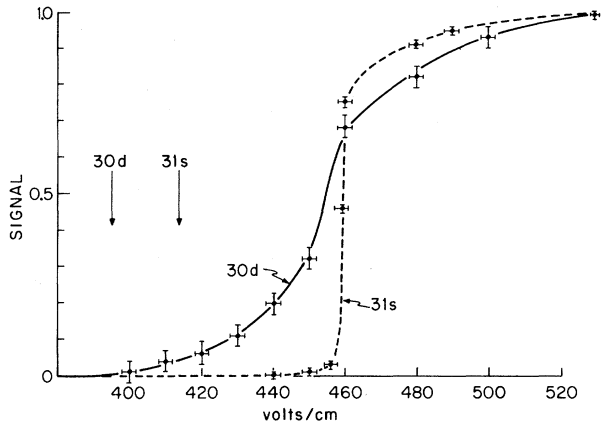

FIG. 2. Ionization signal as a function of the pulsed ionizing electric field. The onset of ionization is broader for the 30d level than for the 31s. This is due to the Stark splitting in the ionizing field of the 30d. The 31s remains a single-shifted level. The vertical arrows indicate the critical ionization field of the unshifted levels from Eq. (1).

to an accuracy of about 1 cm^{-1} and the quantum defects for all n were determined to be $\Delta(s) = 1.35(4)$, $\Delta(d) = 0.00(4)$, in good agreement with the values at lower levels.[6] For $n > 38$ the laser resolution was insufficient to resolve the splitting between adjacent ns and $(n-1)d$ levels, though individual pairs could be resolved to $n = 50$. With a narrower laser line, individual states should be resolved for much higher values of n.

By studying the ionization probability as a function of electric field for different levels we have been able to observe the Stark shift at the onset of ionization. This problem has evoked continued interest over the years because it represents the extreme case of distortion of a free atom by an electric field.[7] Consistent results on the ground state of hydrogen have been obtained by several authors.[8] Huschfelder and Curtiss[9] have considered the $n = 5$ case, in detail, but to our knowledge a complete theoretical treatment for high-n states is lacking.

The alkali system differs from hydrogen in the important respect that the degeneracy of the low-angular-momentum states is broken, regardless of n. This presents a useful experimental advantage, for it allows selection of a single member of an otherwise n-fold-degenerate manifold of angular momentum states. This is illustrated in the data on the ionization threshold shown in Fig. 2. The 31s-state curve exhibits the abrupt onset of ionization that characterizes a single energy level; the width of the curve for the 30d state is attributed to its multiplicity.

The Coulombic potential in an applied field, $V = -1/r - Ez$ (a.u.) has a maximum $V_{max} = -2\sqrt{E}$. The ionization threshold for high-n states is well defined because the range of fields for which tunneling would be observed is extremely narrow. Ionization occurs when $V_{max} = W_n$, where W_n is the term energy. If we neglect the Stark effect, then $W_n = -[2(n^*)^2]^{-1}$, and the threshold field would be

$$E_n{}^0 = [16(n^*)^4]^{-1}. \quad (1)$$

We have measured the critical ionization fields, E_n, for s levels with $n = 26$–37. The results of Eq. (1) and the data are compared in Fig. 3. E_n is consistently larger than $E_n{}^0$. This difference arises because of the Stark shift.

A simplified analysis of the critical-field data can be made by assuming the wave function remains essentially Coulombic at the ionization threshold. We can write the term energy at threshold as

$$W_n = W_n{}^0 + \delta W_n, \quad (2)$$

where $W_n{}^0 = -[2(n^*)^2]^{-1}$, and δW_n is taken as the Stark shift at ionization. Values for δW_n may be extracted from the data in Fig. 3 using the relation

$$\delta W_n = -2\sqrt{E_n} - W_n{}^0. \quad (3)$$

An estimate of the Stark shift can be obtained by assuming that the ns state mixes chiefly with the np state. With this two-level model we calculate values for the Stark shift at ionization which are in general agreement with the values

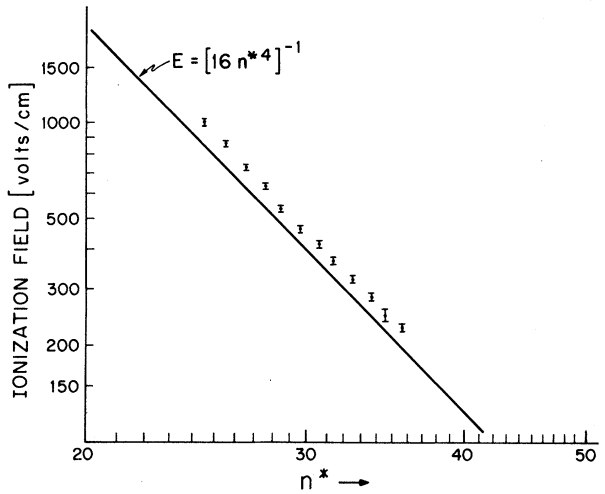

FIG. 3. Log-log plot of critical ionization field versus n^* for $n = 26$–37. The straight line represents the predictions of Eq. (1) for no Stark shift. The actual critical field is consistently larger than the prediction. This is a result of the Stark shift at ionization.

extracted from the data, but are typically 30% low. For example, at $n = 30$, $\delta W_n = 5.6 \times 10^{-5}$ a.u. from Eq. (3), and 4.0×10^{-5} a.u. from the two-level analysis. More precise measurements and more realistic calculations which consider the contribution to the Stark shift of all important states are in progress.

The technique described here should be useful for studying a variety of other problems involving highly excited atoms. In addition to questions of polarizabilities and tunneling phenomena, there is interest in the behavior of atoms when the magnetic energy dominates the Coulomb energy[10] and in photoionization and other radiation phenomena. The technique of high-level excitation and ionization provides a selective way to detect excited atoms with very high efficiency and virtually no background. It may also have useful applications in a photon detector.

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†A preliminary report of our work has appeared: T. W. Ducas, M. L. Littman, R. R. Freeman, and D. Kleppner, Bull. Am. Phys. Soc. 20, 680 (1975).

[1]A. K. Dupree and L. Goldberg, Annu. Rev. Astron. Astrophys. 8, 231 (1970).

[2]T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. A 11, 1504 (1975).

[3]J. E. Bayfield and P. M. Koch, Phys. Rev. Lett. 33, 258 (1974); P. M. Koch and J. E. Bayfield, Phys. Rev. Lett. 34, 448 (1975).

[4]T. B. Cook, W. P. West, F. B. Dunning, and R. F. Stebbings, Bull. Am. Phys. Soc. 20, 253 (1975).

[5]T. W. Hansch, Appl. Opt. 11, 895 (1972).

[6]C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. GPO, Washington, D. C., 1949), Vol. 1.

[7]The early work is summarized in H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic, New York, 1957).

[8]J. B. Mendelsohn, Phys. Rev. 176, 90 (1968); M. H. Alexander, Phys. Rev. 178, 34 (1969); J. D. Bekenstein and J. B. Krieger, Phys. Rev. 188, 130 (1969).

[9]J. O. Hershfelder and J. A. Curtiss, J. Chem. Phys. 55, 1395 (1971).

[10]See for example V. W. Hughes and R. O. Mueller, in *Fourth International Conference on Atomic Physics, Heidelberg, Germany, 1974. Abstracts of Contributed Papers*, edited by J. Kowalski and H. G. Weber (Heidelberg Univ. Press, Heidelberg, Germany, 1974), p. 104; also R. F. O'Connell, *ibid.*, p. 145.