tential-energy-curve crossing at 24.6 eV reported by Brenot *et al.* (This crossing leads to a $3p^54p$ excited Ar atom which could, via a cascade process, contribute to the observed uv emission.) Furthermore, the true energy threshold must be only 11.6 eV, the excitation energy of the lowest $3p^54s$ resonance level of the Ar atom.

The basically exponential energy dependence of the reported uv emission cross section, as given by Eq. (2), is perhaps suggestive of a quantum-mechanical barrier-penetration phenomenon, with transitions occurring at somewhat larger separations than the crossing radius. Of course, such transitions between the molecular potential energy curves at radii beyond the crossing vicinity remain energetically possible down to 11.6 eV.

If the interpretation that photons are being observed at energies below the crossing energy is correct, it points to the danger of establishing curve-crossing radii from threshold-energy determinations. If it is not correct, then it would appear that the crossing responsible for the observed uv emission has been improperly identified.

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*This work constitutes a portion of the Ph.D. thesis of H. L. Rothwell, Jr., University of Denver, 1975.

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Structure of Sodium Rydberg States in Weak to Strong Electric Fields*

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We present results of an experimental survey of the $n = 15$ state of Na in electric fields from 0 to 4 kV/cm. Both linear and higher-order Stark effects play important roles. States with low $|m|$ show marked differences from hydrogenic behavior, particularly in the vicinity of level crossings. Computed values for the energy levels are in good agreement with the data. The experimental method provides a simple technique for populating selected Stark or angular momentum levels of a Rydberg state.

A number of research groups have now developed techniques for creating and detecting atoms in pure Rydberg states,[1] opening the way to studies in such areas as electron-core interactions, tunneling and photoionization phenomena, correlated electron motion, and collisions. For many applications it is essential to populate selected angular-momentum states or, in the case that an electric field mixes angular momentum, to populate selected Stark states.[2] We present here re-

sults of a study of some Rydberg states of Na which display the systematics of Stark structure and which demonstrate the feasibility of populating preselected components of a Stark manifold.

The starting point for describing the Stark structure of a Rydberg state of an atom in an electric field is the first-order expression for the energy of hydrogen,[3] $W = W_0 + W_1$, where $W_0 = -\frac{1}{2}n^2$ a.u. is the unperturbed term energy and W_1 is the first-order Stark energy. $W_1 = \frac{3}{2}n(n_1 - n_2)E$, where E is the electric field, n is the principal quantum number, and the parabolic quantum numbers n_1 and n_2 satisfy $n_1 + n_2 + |m| + 1 = n$. m is the usual azimuthal quantum number. (We neglect fine structure, which plays no important role in this work.) For $n = 15$, the separation between the outermost Stark levels is given by $2.6 \times 10^{-2} E$ cm^{-1}, where E is in volts per centimeter.

At electric fields $E > W^2/4$, tunneling phenomena are known to be important[4] and the levels become broadened. We restrict ourselves to fields below this value. Here the Stark splittings are essentially linear, though second- and third-order effects produce slight nonlinearities. Perturbation theory yields accurate results in low fields.[3] As W_1 approaches the term separation, however, perturbation theory breaks down completely. Levels with identical m obey the no-crossing theorem, and the levels of each term are repelled by those of adjacent terms. The matrix elements which couple the crossing levels vary by orders of magnitude depending on the relative slopes of the levels. The particular character of the anticrossings can have important practical consequences if the electric field varies in time, as in field-ionization experiments where the ionization-threshold field is used as a signature for the state of the atom. Oppositely sloping levels in hydrogen are so weakly coupled that in practice the crossings are always traversed diabatically. In contrast, intermediate components of a Stark manifold may be so strongly repelled that the crossings are essentially adiabatic. It is apparent that care is needed in establishing the correspondence between high- and low-field states.

In the case of an alkali the term energy is given by $W_n = -\frac{1}{2}(n - \delta_l)^2$, where δ_l is the quantum defect. The energy of each term is lowered from the hydrogenic value by $\delta W \cong \delta_l \Delta W_0$, where $\Delta W_0 \cong n^{-3}$ is the zero-field separation of adjacent terms. The low–angular-momentum states are displaced from the Stark manifold and at low fields they display second-order Stark shifts. The remaining degenerate states display a first-order Stark splitting, but unlike the hydrogenic case the submanifolds with even and odd $|m|$ may coincide. (In hydrogen the even and odd manifolds are staggered.) As the field increases, the low–angular-momentum terms merge into the linear manifold and the $|m|$ degeneracy is removed.

Many of the features described above are evident in the experimental results of Fig. 1(a). The data consist of excitation curves for Na in a static electric field obtained with apparatus described elsewhere.[5] Atoms in a beam were stepwise excited by radiation from two pulsed tunable lasers. The first laser excited the 5889-Å transition $3^2S_{1/2} \rightarrow 3^2P_{3/2}$. The second laser was tuned to approximately 4150 Å and excited transitions to high-lying states in the vicinity of $n = 15$. This laser was linearly polarized parallel to the applied electric field and the selection rule $\Delta m = 0$ restricted final states to levels with $|m| = 0$ or 1. The maximum field, 4 kV/cm, lies well below the field for which tunneling was first observed, 5.5 kV/cm. 1 μsec after the laser pulse, a field of ~ 15 kV/cm was applied which ionized all the Rydberg-state atoms. The data in Fig. 1(a) were obtained by scanning the second laser and recording the ionization current at a series of increasing fields. The natural width of the levels is negligible compared to the laser linewidth, 0.5 cm^{-1}, and the shape of the excitation peaks reflects the laser line shape. The intensity of excitation cannot be read reliably from the curves because of saturation in the ion detector. The Stark shift of the initial state, $3^2P_{3/2}$, is negligible, so that Fig. 1(a) gives a true map of the energy levels of the highly excited states.

At zero field, excitation from the $3p$ state occurs only to s and d states, in accordance with the dipole selection rule $\Delta l = \pm 1$. Because of its small quantum defect, $\delta_2 = 0.014$, the d state is practically degenerate with the states $n = 15$, $l > 2$. As the field is increased the linear Stark structure of the submanifold of these states becomes manifest. The large quantum defect of the s states, $\delta_0 = 1.35$, gives them second-order Stark shifts. The $16p$ state, inaccessible at $E = 0$, is excited for $E > 0$ via Stark mixing, chiefly with the nearby $15d$ state. The p state also has a large quantum defect ($\delta_1 = 0.85$) and displays a second-order shift.

At $E = 2$ kV/cm the $16s$ level sharply repels the lowest $m = 0$ component of the $n = 15$ linear sub-

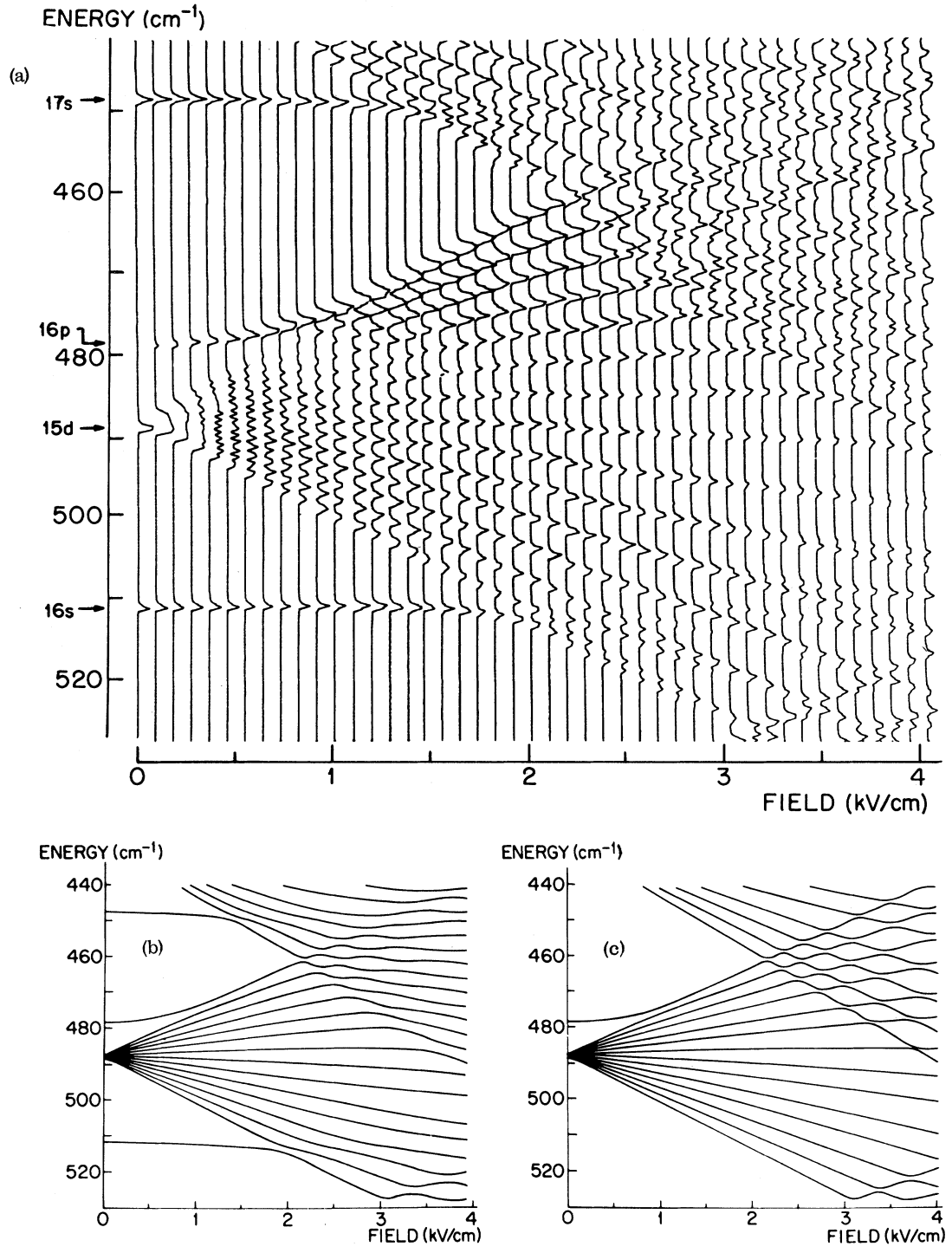

FIG. 1. Stark structure of Na. (a) Experimental excitation curves for Rydberg states of Na in the vicinity of $n = 15$. A tunable laser was scanned across the energy range displayed (vertical axis). The zero of energy is the ionization limit. A signal generated by ionizing the excited atoms appears as horizontal peaks. Scans were made at increasing field strengths (92 V/cm increment) and are displayed at the corresponding field values. Both $|m| = 0$ and 1 states are present. Arrows identify zero-field position of levels nl. (b) Calculated energy levels for the $|m| = 0$ states displayed above. (c) Calculated energy levels for the $|m| = 1$ states displayed above.

manifold, but the $|m| = 1$ components are unaffected. The result is an apparent branching of the lowest state of the submanifold. A number of similar branch points can be seen in Fig. 1(a) which collectively break the degeneracy of the $m = 0$ and $|m| = 1$ levels.

The level structure observed in Fig. 1(a) has been accounted for quantitatively by diagonalizing the energy matrix for $n = 14$, 15, 16, and 17, with the addition of the 18s and 18p states. Results are shown in Figs. 1(b) and 1(c). For high-angular-momentum states, hydrogenic dipole matrix elements were used. Matrix elements for the low-angular-momentum states were generated numerically by integrating the radial equation using a Numerov alogorithm based on a logarithmic grid. We have obtained excellent agreement between the calculated and observed energies for all the data displayed in Fig. 1. A detailed account will be published elsewhere.

The low-$|m|$ states of Na display a Stark structure dramatically different from hydrogen. A diagram for hydrogen corresponding to Fig. 1(b) shows such sharp crossings between oppositely sloping levels that no repulsion is evident. Physically this is because wave functions for states with opposite Stark shifts are concentrated in opposite directions along the electric field, yielding a negligible value for the matrix element of $\vec{E}\cdot\vec{r}$ coupling the two states. In contrast, Fig. 1(b) shows that the s and p states in Na strongly repel the linear Stark states for the terms lying above and below, creating a formidable barrier between those terms. Even though the dipole moments for the linear Stark states in Na closely resemble their hydrogenic counterparts, the small distortions in the wave functions arising from the effect of the atomic core on the s- and p-state components result in a matrix element in Na which is relatively large. The effect is much less noticeable for the $|m| = 1$ state, where only the p-state distortions are important [Fig. 1(c)]; the higher-$|m|$ states rapidly approach hydrogenic behavior.

The techniques employed here open the way for studying the systematics of interactions among Stark states. Line intensities can give a measure of oscillator strengths for transition to low-lying levels, while level repulsions provide sensitive tests of interactions between Stark levels. By sweeping the electric field through a crossing region at various rates, the dynamics of level-crossing transitions[6] can be studied. Furthermore, the techniques are useful for populating levels which are normally inaccessible from the ground state. For instance, if we consider atoms with $Z > 1$, the zero-field l degeneracy is broken by core-polarization effects, and each of the linear Stark states connects adiabatically to a single angular momentum state. By exciting the atom in an electric field in which the first-order structure is resolved and then reducing the field to zero, states with any desired value of l can be populated. At the other extreme, by exciting the levels in a high field, the ionization properties of individual Stark levels can be studied. We are currently pursuing a number of these applications.

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