Continuum Stark Spectroscopy

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We observed well-resolved spectral features in the stepwise ionization of Na in an applied electric field near the zero-field ionization threshold. A 5890-A pulse excites atoms to the 3^2P state and a ~4085-A pulse, swept through threshold ionizes them. Using the method of Luc-Koenig, we calculated the oscillator strength density versus blue laser frequency and compared it with our data. The agreement is excellent. Parabolic quantum numbers have been assigned to the spectrum and the Fano profiles have been analyzed.

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Before quantum mechanics it was known that the problem of a hydrogen atom in an electric field is separable in parabolic coordinates.[1] Recent developments of numerical methods[2,3] and WKB calculations[4] to solve accurately for the parabolic wave functions and energies near the (zero-field) threshold E_0 have been stimulated by experiments in Rydberg atoms[5-7] for which ordinary laboratory fields can dominate the Coulomb binding interaction. Comparison of these results with measurements[7] of Stark shifts of quasidiscrete levels below E_0 show that direct numerical solution compares well with both data and more sophisticated perturbation[8] and group-theoretical[9] methods. In addition, similar computations corroborate spectral structure that has been observed in single-photon ionization of Rb (Ref. 10) above E_0 where the ion core presents a nearly pure hydrogenic Coulomb potential. These calculations[2] suggested that above E_0 the crucial quantity was the oscillator-strength density (OSD) that could vary significantly within a broad quasiresonance, rather than simply the density of states. However, predictions for photoionization of excited states extrapolated from these calculations were contradicted by observations,[11] lending support to earlier arguments based on classical[10] or semiclassical[12] models.

This paper reestablishes the correctness of the method developed by Luc-Koenig and Bachelier[2] by more extensive comparisons with observations of stepwise ionization of Na through the $3P$ states. Furthermore, we find the predictions for photoionization from excited states to be inconsistent with explicit calculations in parabolic coordinates. The position and amplitude of resonances below E_0 and undulations above it now agree well with theory.

Such calculations on hydrogenic systems[2] do not include interaction with the ion core that may produce significant qualitative effects in the spectra.[13] These are manifest in our experiments as Fano line-shape profiles that appear even more prominently than in previous reports on Rb photoionization.[14] We attribute these profiles to coupling by the non-Coulomb part of the core potential between "sharp" states of specific n_1 quantum number with continuum states of lower n_1 values.

In our experiments sodium atoms in a thermal beam are stepwise ionized by two laser pulses (one tuned to D-line excitation) in a constant electric field. The first laser prepares a $3P$ state and the second, which is swept through threshold, ionizes the atom. We use various combinations of linearly polarized light (e.g., $\sigma\pi$ means polarization of the first laser is perpendicular to $\vec{E}$ field and the second one is parallel to $\vec{E}$ field). The dye laser pulses were of ~ 10 nsec duration, essentially simultaneous, and repeated at 12 Hz. The wavelength was measured to ± 0.3 cm^{-1} with a precision etalon calibrated with the H atomic line at 4101.7 Å. The laser beams intersected the atomic beam between two field plates spaced about 0.7 cm apart, one of which was a 75% transparent mesh. The Stark field accelerated photoelectrons through this grid into a multichannel plate where they were detected with very high efficiency. The applied voltage measurements were accurate to 0.2%, the plate spacing was measured to 1%, the field is therefore known to about 1%, and its inhomogeneity in the interaction region is estimated to be less than 1%. There was no ionizing pulse so that we only observed "states" that field ionize at rates greater than about 10^5/sec. Typical scans (Figs. 1 and 2) show spectral structure in the production of photoelectrons as the frequency of the photoionizing laser was swept through about 100 cm^{-1} ($\lambda \cong 4085$ Å, linewidth $\cong 0.2$ cm^{-1}). Field changes produced shifts of the spectra in agreement with our calculations.

Theoretical studies of Stark structure for $n \sim 15$ and fields up to ~ 8 kV/cm in alkali atoms[13] have

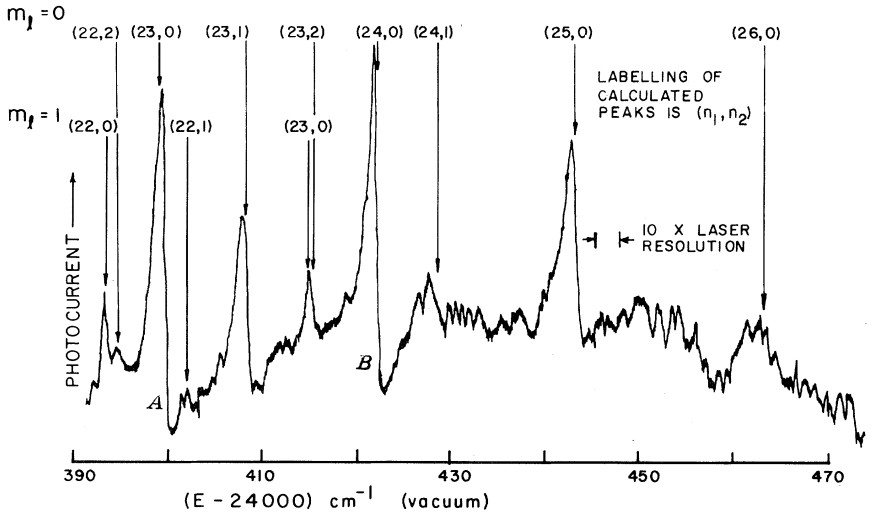

FIG. 1. Spectral scan just below the zero-field ionization limit of the $3^2P_{3/2}$ state of sodium. Parabolic-quantum-number assignments and peak positions are derived from calculations discussed in text. The peak positions may be shifted by the Fano interference (up to one-half linewidth) or the 1% field uncertainty (up to 2 cm^{-1}). Note the well-defined Fano profiles.

shown that perturbation theory in a spherical basis leads to accurate agreement with experiment. The effect of the core was adequately included by numerical integration of the basis wave functions at the experimental (quantum defect) energies. At higher energies and fields it is better to treat the core potential rather than the external field as a perturbation and solve by separating the Schrödinger equation in parabolic coordinates η and ξ.[1,15] The motion in ξ is bounded and leads to an eigenvalue problem with eigenvalue Z_1, the parabolic separation constant (solutions exist for all values of E for nonzero applied field.) The motion in η is unbounded but involves barrier tunneling for E less than the parabolic critical energy, E_c^p, a function of m, n_1, and the applied field F.

We calculate the energy dependence of the OSD by finding the separation parameter Z_1 of the ξ equation for a given final-state energy and using it to find the η function by numerical integration. Then the electric dipole transition probability from the 3^2P state is calculated with this final-state wave function. The Na $3P$ wave function is computed in spherical coordinates by numerical integration inward from infinity at the experimental energy,[13] and then transformed to parabolic coordinates. The OSD is plotted against energy for each value of the parabolic quantum number, n_1, the number of nodes in the ξ function. We distinguish the contributions from various values of n_2, the number of nodes in the η function, between the origin and the η potential maximum. Figure 3 shows our calculated OSD for $F \cong 3.59$ kV/cm, $m = 0$ and 1, for various n_1 values. There are broad resonances above E_c^p which narrow with decreasing field and/or energy and eventually sharpen into the well-defined states of Ref. 13 at low enough fields. The sharpest resonances have lowest values of n_2 for fixed n_1 because they are highest in energy for given $n = n_1 + n_2 + |m| + 1$; the electron distribution is furthest to the cathode side of the nucleus. These calculations are used to assign quantum numbers to the peaks in Figs. 1 and 2.

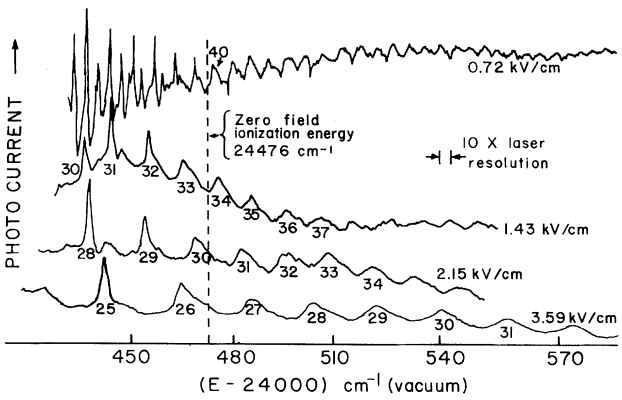

FIG. 2. Spectral scan similar to Fig. 1, but shown for several field values and covering a wider energy range, including energies well above E_0. At low fields the resonances begin to look like the Rydberg Stark states of Ref. 13.

To account for the fine structure we compute the 3^2P density matrices in an $m_l m_s m_I$ basis because the first (yellow) quantum produces a mixture of $m_l = 0$ and 1 sublevels. The continuum density matrix is diagonal in $m_l m_s m_I$ because of the very weak coupling between l, S, and I in the continuum states and because all electrons are detected. Hence the total spectrum is the sum of $\Delta m = 0$ transitions ($m_l = 0$ and 1) for π polarization and of $\Delta m = \pm 1$ transitions for σ polarization of the second (blue) quantum. Near and above threshold, most of the observed structure occurs only in $m_l = 0 \rightarrow 0$ transitions.

The effects of the sodium ion core are manifest in the Fano line profiles[14,16] with a characteristic dip on one side of a resonance. Such profiles are a very general property of alkali atom photoionization spectra in an electric field, as shown by peaks at 24 405 and 24 428 cm^{-1} in Fig. 1. The Fano profile A in Fig. 1 comes from mixing by the core potentials of the $n_1 = 23$, $n_2 = 0$ "sharp" peak with $n_1 = 22$ and 21 continua. A complication here is that the "sharp" peaks have typically finite widths themselves, and in some cases the laser linewidth must also be considered. The measured Fano parameters[16] [$q = 1.7(0.3)$, $\Gamma = 0.7(0.15)$ cm^{-1}, for the B peak] must be interpreted with these considerations in mind. These shapes provide useful tests for the inclusion of core effects into the photoionization theory, since quantum number assignments and accurate zeroth-order wave functions are available.

We can make a detailed correspondence between the experimental peaks in Fig. 1 with peaks calculated with the hydrogenic model, as shown in Fig. 3. The agreement in peak positions is excellent; in most cases it is within the accuracy of the field calibration. The values of the Fano parameters remain to be calculated.

With good agreement between experiment and theory below E_0, we now study the undulations above E_0. The first observations of these undulations[5] have prompted a variety of theoretical interpretations.[2,4,10,12] Our observations contradict most predictions based on simplified models, but substantiate the detailed calculations described above.

The percent modulation amplitude in Fig. 2 is about the same [$(6 \pm 2)\%$] for $\pi\pi$ and $\sigma\pi$ laser polarizations, and for $3^2P_{1/2}$ and $3^2P_{3/2}$ intermediate states. No modulations are observable (amplitude $< 2\%$) for $\pi\sigma$ and $\sigma\sigma$ polarizations. Hence it cannot be said that modulations appear whenever $m = 0$ "quasiresonances" above E_0 are excited,[10] nor that the undulations obey quantum-number selection rules based on reflection symmetry in

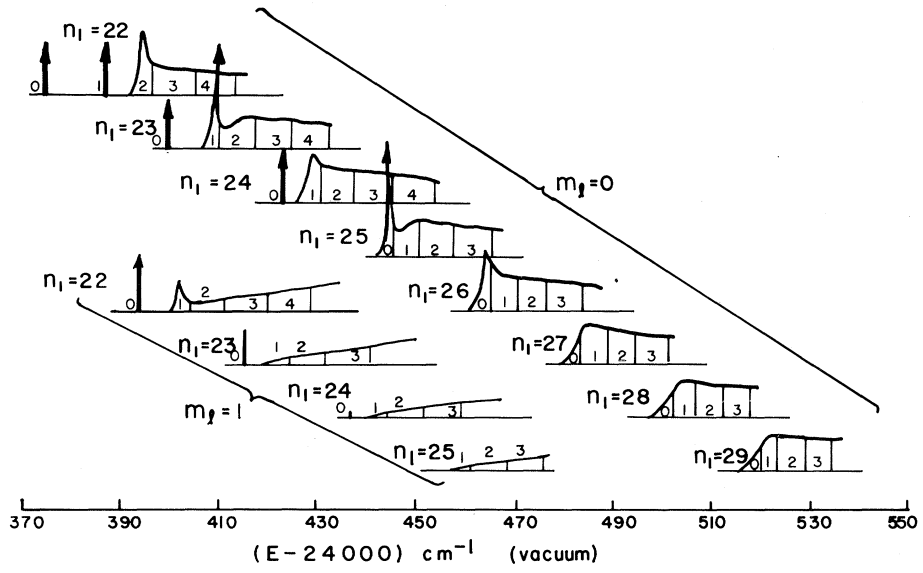

FIG. 3. Calculated values of oscillator strength density at 3.59 kV/cm for the transitions studied here. Note the narrowing of the resonances to sharp transitions at low fields and/or energies. Comparison of this with Figs. 1 and 2 makes it clear how the parabolic quantum numbers are assigned. The relative strengths of the $1 \rightarrow 1$ and $0 \rightarrow 0$ parts depend on the excitation process. The small numbers refer to the n_2 region within each n_1 manifold. These are sharply defined because n_2 is equal to the number of nodes in η function between the origin and the potential maximum.

the x-y plane.[2] Instead the peaks are associated with sharp maxima in the OSD. Our calculations, confirmed by experiment, show that modulations appear only for $m_l = 0 \rightarrow 0$ transitions. The peaks are associated with low values of n_2, but not always precisely with $n_2 = 0$, nor with $Z_1 = 1$, $Z_2 = 0$.[4]

The distinction between maxima in the density of states and maxima in the OSD can be clarified by a simple analogy. Consider transitions from a localized state to states of an electron in a uniform electric field (Airy functions). The transition strength oscillates with energy as the nodes of the Airy function scan pass the origin. However there are no resonant states associated with these OSD maxima. The addition of a central Coulomb field introduces a strong constraint at the origin so that nodes now do not scan through the origin continuously. Nevertheless, for a given number of nodes (n_1) between the origin and the classical turning point, there is one prominent peak in the transition strength as shown in Fig. 3, whereas the density of states simply rises to a broad flat maximum.[2]

Undulations appear only for $m_l = 0 \rightarrow 0$ transitions because these wave functions are most concentrated along the z axis, where they have a succession of nodes. The nodes move as a function of energy, and new ones appear as n_1 changes, so that the transition strengths from lower $m_l = 0$ states exhibit sharp maxima. For $m_l = 1$ states, ψ is everywhere zero along the z axis and the transition integrals entail considerable spatial smoothing of the interference effects. The resultant peaks are so broad that there is only a negligible modulation in the total transition probability.

In summary, we have observed well-resolved spectral features in the stepwise ionization spectrum of sodium just below the zero-field threshold, and marked oscillations above it. The intensities and peak positions agree well with hydrogen calculations of the OSD, and Fano line profiles appear because of core coupling between hydrogenic channels.

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