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CONTINUUM STARK SPECTROSCOPY

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Résumé - Nous présentons l'étude expérimentale et théorique de la photoionisation par échelon via l'état 3P du sodium dans des champs électriques jusqu'à 3,90 kV/cm. L'appareillage utilise un jet atomique et l'excitation est réalisée à l'aide de deux lasers pulsés dont les faisceaux sont orthogonaux au jet atomique. Le premier laser à 589 nm permet l'excitation des niveaux P. Le second laser autour de 409 nm permet la photoionisation autour de la limite d'ionisation $E_0$ en champ nul. Nous avons observé des ondulations de grande largeur dans le courant photoélectrique au-delà de $E_0$. Leur largeur décroît lorsque l'énergie décroît. Dans certains cas elles s'affinent en des raies bien définies mais asymétriques correspondant aux états de Rydberg déplacés par effet Stark. Nous avons calculé la densité de force d'oscillateur pour ces transitions en utilisant des fonctions d'ondes hydrogénoïdes modifiées. L'accord avec les résultats expérimentaux est excellent. Nous avons considéré les asymétries comme le résultat d'interférences de Fano entre la partie quasi-discrete du spectre et les canaux d'ionisation. En utilisant des potentiels du coeur appropriés, et en tenant compte du couplage entre états discrets-continus et continus-continus induits par l'interaction avec le coeur, nous avons obtenu des valeurs $q$ et $\gamma$ des paramètres de Fano en bon accord avec nos mesures.

Abstract - We have studied experimentally and theoretically two-step photoionization through the 3P state of sodium in an electric field of up to 3.90 kV/cm. The apparatus uses an atomic beam crossed by two pulsed laser beams, one at 589 nm for the first step, and the other swept through the zero field threshold $E_0$ near 409 nm for the ionization. We observe broad undulations in the photocurrent above $E_0$ that narrow with decreasing energy and eventually sharpen into well-defined but asymmetric transitions to Stark-shifted Rydberg states. We calculate the oscillator strength density for the appropriate transitions using modified hydrogenic wave functions and find excellent agreement for the position and relative strength of all the spectral features. We model the asymmetries as Fano-type interferences between quasi-discrete and continuum ionization channels. Using appropriate core potentials, and taking into account core-induced coupling of both discrete-to-continuum and continuum-to-continuum states, we obtain estimates of Fano's $q$ and $\gamma$ that agree reasonably well with our measurements.

1. Introduction. - Studies of the energy levels of atoms in external electric fields have undergone increased vigor and activity during the last several years. The advent of tunable dye lasers that can easily excite levels of high principal quantum number $n$ having high electric field sensitivity has allowed the experimental investigation of the Stark effect in a previously inaccessible domain. There are two major reasons for the extraordinary sensitivity of these levels to electric fields: 1) the states are characterized primarily by atomic binding fields that may easily be $10^5$ times weaker than those of lower-lying levels, and 2) there are very closely lying levels of opposite parity that are readily mixed by the electric field thereby allowing large induced dipole moments that enhance the strength of the interaction with the external field. The result is observable Stark shifts in...
ordinary laboratory fields (few kV/cm) that amount to hundreds of cm\(^{-1}\) in the optical spectrum where tunable lasers have resolution much better than 1 cm\(^{-1}\). In fact, the principle experimental limit to precision Stark spectroscopy is presently the production and measurement of the electric fields themselves.

The usual theoretical description of the Stark effect, by perturbation theory applied to the familiar spherical solutions of the Schroedinger equation, is rapidly pushed beyond the limit of validity by experiments on alkali atoms near threshold because of the vast number of high-lying states that are coupled by the field. However, for a purely 1/r central potential and a uniform electric field (the hydrogen atom Stark effect), the Schroedinger equation is separable in parabolic coordinates [1]. The resulting one-dimensional equations are solvable by numerical methods. There are no true bound states because at a sufficiently large distance in the direction of the field the electron has penetrated a potential barrier and is no longer bound to the atom. Therefore energy does not have discrete eigenvalues and wave functions exist for all values of energy (though with widely varying amplitude at the origin.) Nevertheless, two of the three ordinary differential equations that separate out in parabolic coordinates have discrete eigenvalues. The first such equation is the same as in spherical coordinates and gives the familiar magnetic eigenvalue \(m\) and the solutions \(\psi = e^{i m \phi}\). The eigenvalue of the second equation is not related to familiar physical quantities such as \(m\) or \(l\) (angular momentum), but to the number of nodes, \(n_1\), on the upfield side of the nucleus. The eigenvalue is actually the separation constant \(Z_1\), which varies from 0 to 1 for states of interest; \(Z_1 \approx (n_1 + \frac{1}{2} + \frac{1}{4} |m|)/n\). From the numerically computed solutions one can calculate physical observables in the usual way. For example, optical transitions can be described in terms of the well known electric dipole and rotating-wave approximation. From near the zero-field threshold and above, these hydrogen Stark wavefunctions provide a good first approximation to alkali atom Stark effects. Some significant exceptions arising from the presence of the core are discussed below.

Figure 1 shows that the sum of the Coulomb binding potential and the external

![Figure 1](image)

Figure 1. The combination of Coulomb and uniform fields produces a potential well having bound states degenerate with unbound ones. Parabolic states are subject to an additional effective potential (dashed line) that may bind states with energy greater than \(E_c\).

Stark potential produces three energy regions, separated by the zero-field ionization potential \(E_o\) and the classical field ionization point \(E_c = -2\sqrt{F_p}, F_p = 1/(16n^4)\)[2,3]. At first thought it might seem that there are quasi-bound states below \(E_c\) and continuum states above it. However, the separation in parabolic coordinates produces an additional potential \(V_p\) that is analogous to the centrifugal potential in
spherical coordinates. For the downfield side of the nucleus, \( V(z) = Z_1/z + (m^2 - 1)/8z^2 \) (for \( x=y=0 \)). From the above expression for \( Z_1 \), it is seen that \( V_0 \) increases for \( n_1 > 0 \) so that states of high \( n_1 \), up to \( n-m-1 \), may still be bound even though they are far above \( E_0 \) (see Fig. 1). For a given \( n = n_1 + n_2 + |m| + 1 \), those states highest in energy (maximum \( n_1 \)) lie farthest to the cathode side and ionize most slowly. Thus between \( E_c \) and \( E_0 \), there coexist many nearly uniform continua of states, along with broad and sharp quasi-bound states, (instantaneous, fast, and slow ionization rates) depending on the effective "parabolic" potentials \( V_0 \). Above \( E_0 \) there are no resonant states but under certain conditions outlined below, one observes broad undulatory spectral structure. All of these states arise from the same Hamiltonian and may be computed by the same methods. They differ only in their ionization rate, depending on their position relative to the effective potential barrier in the third parabolic variable.

2. Experimental Description.— In our experiments (see figure 2) 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, swept laser ionizes the atom. We use various combinations of linearly polarized light (e.g., \( \sigma \pi \) means polarization of first laser is \( \perp \) to \( E \) field and second one is // to \( E \) field). The dye laser pulses were of \( \sim 5 \) nsec duration, essentially simultaneous, and repeated at 12 Hz. The wavelength was measured to \( \pm 0.5 \text{ cm}^{-1} \) 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 ionization pulse so that we only observed "states" that field ionize at rates greater than about \( 10^5 \) Hz.

Typical scans (figures 3 and 4) show spectral structure in the production of photoelectrons as the frequency of the photoionizing laser was swept through about

![Figure 2. The energy levels used in the experiment are shown at the left. The core of the apparatus is shown at the right. The laser beams and atomic beam intersect near the bottom plate where the field homogeneity is best. Electrons are accelerated upward.](image-url)
Figure 3. Part of the spectrum at 2.15 kV/cm showing broad undulations above $E_o$ and narrow features below $E_o$.

Figure 4. Part of the spectrum at 3.90 kV/cm showing the calculated positions of the peaks. Note the asymmetric line shapes and the resulting shift of the peaks. Also note that the $m=1$ peaks are very nearly symmetrical.

100 cm$^{-1}$ ($\lambda \approx 4085\AA$, linewidth $\approx 0.4$ cm$^{-1}$). Field changes produced shifts of the spectra in agreement with our calculations. There are broad features above $E_0$ which narrow with decreasing energy and eventually sharpen into well-defined transitions to Stark-shifted Rydberg states. 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.

The percent modulation amplitude we observe in the undulations above $E_0$ 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. This is consistent with our calculations that show that modulations appear only for $m_L = 0 + 0$ transitions and maxima occur at low values of $n_2$ (but not always precisely with $n_2 = 0$).

3. Theoretical Discussion, $E > E_0$. Some physical insight about the broad features above $E_0$ may be gained by considering the extreme case where the effect of the Coulomb field on the final state is neglected. The wave function for the final state
is then that of an electron in a uniform field: a one-dimensional Airy function characterized by a classical turning point and the uniform potential gradient. Electric dipole transition probabilities depend on the integral of these Airy functions multiplied by the original, low-lying states and the operator \( \hat{T} \). As the energy of the final state is raised by small amounts, its classical turning point shifts and the nodes and antinodes of the Airy function shift past the origin of coordinates where the transition moment integral has its major contribution from the tightly-bound original state. Thus the transition probability oscillates with energy in a simple and calculable way, showing structure in the continuum at energies very much higher than the zero field ionization threshold, \( E_0 \).

Of course, in the region near the origin where the transition moment integral is determined, one cannot neglect the Coulomb potential. The wave function is not the simple Airy function suggested above, but has a cusp as a result of the Coulomb well (see Fig. 5). As the excitation energy is raised, transitions to states of higher \( n_1 \) quantum number are allowed, and new contributions to the wave function appear, each having one more node between the origin and the classical turning point. There still remains some excitation probability to the former state, but its energy dependence is rather weak compared with that of the transition to the newly accessible state. Thus an oscillation in the excitation rate appears with the addition of each new node of the wave function between the origin and the classical turning point.

Undulations appear only for \( m_2 = 0 \rightarrow 0 \) transitions because these wavefunctions are most concentrated along the \( z \) axis, where they have a succession of nodes. The nodes move as a function of energy so that the transition strengths from lower \( m_2 = 0 \) states exhibit sharp maxima. For \( m_2 \neq 0 \) states, \( \psi \) is zero everywhere along the \( z \) axis. The transition integrals entail considerable spatial smoothing of the interference effects if either initial or final state has \( m_2 \neq 0 \). The resultant

![Figure 5. The oscillator strength density depends on the integral of (initial state)\( x \) (transition operator)\( x \) (final state). The product of the first two is plotted on the lowest trace. Other plots show wave functions of a particular \( n_1 \) for various energies along \( z \) axis (units depend on electric field), as well as wave function at one energy for a new \( n_1 \).](image)
peaks are so broad that there is only a negligible modulation in the total transition probability.

These oscillatory features have been observed in atomic spectra and discussed in several recent papers [4-7]. There has even been some disagreement about the appropriate description for this spectral structure in the continuum. Similar features in transitions from bound to continuum states had been predicted [8] as "internal diffraction" effects over 50 years ago, and unambiguously observed [9] in molecular spectra. These undulations are characteristic of excimer emission spectra [10] as well as other molecular transitions [11]. In both the atomic Stark-ionization spectra discussed here and the molecular Franck-Condon oscillations, the spectral structure arises from undulations in the transition probability and not from the presence of resonances in the continuum of final energy states. It is the task of continuum Stark spectroscopy to study the shapes, widths, and positions of these spectral features both above and below \( E_0 \), and to provide a consistent, simple, general description of the observed spectra.

4. Theoretical Discussion, \( E < E_0 \). - More demanding comparisons with data can only be made with careful calculations of appropriate physical observables. Because the spectrum of highly excited atoms in electric fields shows broad as well as sharp transitions, the most natural spectral quantity is the oscillator strength density (OSD) described by Luc-Koenig and Bachelier [12]. In order to calculate this, we first compute numerical final-state wave functions in parabolic coordinates for a Coulomb-plus-Stark field as described above (one coordinate shown in figure 5). We use these with hydrogen-like wave functions for the lower state, appropriately modified for the quantum defect. In our experiments on sodium this is the \( 3^2P \) excited state because we use a two step excitation process. To account for the fine structure of this intermediate state we compute the \( 3^2P \) density matrices in an \( m_m m_I \) basis because the first (yellow) quantum produces a mixture of \( m=0 \) and 1 sublevels. This computation accounts for the polarization of the exciting laser, and assumes statistical population of ground state \( (3^2S) \) sublevels. The continuum density matrix is diagonal in \( m_m m_I \) because of the very weak coupling between \( \ell, S \) and \( I \) in the continuum states and because all electrons are detected.

We calculate the transition moment integral, calculate the OSD for various final states at any given energy, and then plot it for comparison with the data[5]. Typical results, shown in figure 6, demonstrate that the position and approximate intensities of very many of the spectral features calculated this way agree very well with the data shown in figures 3 and 4. Comparably good agreement is found for various polarizations of the exciting light beams. Detailed description of the line shapes, however, requires a more careful specification of the experimental conditions as well as inclusion of the effects of the atomic core electrons on the final state.

More careful examination of the sharp resonances in the sodium photoionization spectrum shown in figure 4 reveals definite asymmetries; there is a clear sharp edge and dip on one side of some of the peaks. The resemblance to the classic Fano [13] profiles found in many ionization phenomena has led us to develop a theoretical model based on interference between transitions to sharp states of specific \( n_1 \) and continuum states of the same energy, but of lower \( n_1 \). This interference is brought about by coupling induced by the non-hydrogenic part of the central potential from the core electrons. Thus, the various components of the OSD at a particular energy shown in figure 6 cannot be simply added incoherently. It is necessary to account for the state mixing produced by the core first, and then to square the sum to calculate the OSD. Such mixing is very much weaker for \( m\neq 0 \) states than for \( m=0 \) because their wave functions are relatively small in the core (non-penetrating orbits). These are responsible for the sharp, symmetrical peaks in Fig. 4. This mixing aspect of the theoretical description constitutes the major difference between the spectrum of hydrogen [12,14] and that of the alkalis.

In Ref. 13 Fano uses the coupling between discrete states and one or more continua, along with relative transition intensities, to derive asymmetric ionization spectral shapes characterized by a width parameter \( \Gamma \) and an asymmetry
Figure 6. 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 energies. The relative strengths of the 1+1 and 0+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 $\eta$ function between the origin and the potential maximum.

parameter $q$. We follow this approach, taking the unperturbed states to be the hydrogen Stark wave functions described above, and the localized sodium ion potential as the interaction term, to calculate $\Gamma$ and $q$ explicitly. We compute the ion core potential from Hartree-Fock sodium ion wave functions [15] and polarizability terms [16]; the result provides accurate values of the sodium S, P, and D quantum defects. In spite of the apparent appeal of this direct use of the ion potential as the coupling between discrete and hydrogenic continuum channels, the result gives parameters $\Gamma$ and $q$ about 10 times larger than those determined by least-squares fitting to our experimental line shapes. Although other kinds of calculations can be done [17], we have chosen to pursue this one further.

This approach fails badly because it neglects the coupling between different continua and between different energy eigenfunctions within each continuum. To improve the approximation, we "prediagonalize" the continuum channels by means of the Lippmann-Schwinger integral equation,

$$\psi_{n_1}(r) = \psi_{n_1}(r) + \int dr' G(z,z') V(z) \psi_{n_1}(r)$$  \hspace{1cm} (1)$$

with a Green's function that includes all continuum channels but omits the quasi-bound state. The Green's function is

$$G(\xi\eta;\xi'\eta') = e^{im(\phi-\phi')/2} \frac{\sin(n_\eta z)}{n_\eta z} \frac{\sin(n_\eta' z')}{n_\eta' z'} / 2\pi \sqrt{\xi' \eta' - \xi^2}$$  \hspace{1cm} (2)$$
Here the sum runs over $j$ from $n_1=0$ to $n_1=n_1-1$. $F(\xi)$ and $G(\eta)$ are solutions of the equations obtained by separating the Schrödinger equation in parabolic coordinates $\xi$ and $\eta$. The wave function is $\psi(n_1,n_2,m) = F(\xi)G(\eta)e^{i\text{m} \phi/\sqrt{2\pi \xi \eta}}$, normalized to an outgoing wave of amplitude $1/2\pi$. $\phi(\eta)$ is shifted $90^\circ$ from $G(\eta)$ in the asymptotic region, beyond the barrier in the $\eta$ potential. The integral equation (1) is solved for each continuum channel by the Fredholm matrix inversion procedure [18] because the Born series does not converge. A variable mesh grid in the $\xi-\eta$ plane with $\sim 100$ points within an effective core radius of 3 atomic units yields nearly convergent values for the coupling elements between the quasi-discrete and continuum channels. The theoretical value for $\Gamma$ is found by summing the squares of the coupling elements, and results are shown in Table 1 for three resonances. Differences between the calculated and experimental $\Gamma$ values in Table 1 are attributed to the laser linewidth (0.5 cm$^{-1}$) and scanning time constant, which were not considered in the fitting process. These widths can not be simply combined because of the asymmetric line shapes.

The computation of $q$ entails a calculation of the transition moments from a lower state for each "prediagonalized" continuum channel; the integration extends out to 30 a.u. Then $q$ is found from $q^{-1} = \sum q_i^{-1}$. Table 1 indicates that calculated and experimental values of the asymmetry parameter $q$ agree well.

| $n_1,n_2,m$ | Experimental $q$ | Calculated $\Gamma$ | $|q|$ |
|------------|------------------|---------------------|------|
| 22,0,0     | 1.13(15) cm$^{-1}$ | -2.65(30)           | 0.70 cm$^{-1}$ | 2.87 |
| 23,0,0     | 0.86(15)          | -2.75(30)           | 0.60 | 2.91 |
| 24,0,0     | 0.86(15)          | -3.78(30)           | 0.33 | 2.77 |

5. Summary - In summary, we believe that we have established a good theoretical description of the spectrum of transitions to highly excited states in external electric fields that are comparable to or stronger than the atomic binding field. The basis for this theory was outlined in Ref. [12], but we have modified it in two substantial ways. First, we have calculated the OSD for transitions from an excited state to the continuum in order to apply it to our experimental stepwise excitation. Second we have included some of the effects of the atomic core, absent from the hydrogen atom, in order to account for our asymmetric signal shapes. We have made careful measurements of the spectrum of transitions to ionizing states in sodium in external electric fields of appropriate strength. The calculated spectral parameters are in good agreement with our measurements.

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References


3. We use atomic units: $e = m = \hbar = 1 = \omega_0$, unit of electric field = $5 \times 10^9$ V/cm, unit of energy = $2R = 2.2 \times 10^5$ cm$^{-1}$.


17. As an alternative, we could simply calculate the photoionization probability vs. wavelength and fit the resultant lineshape to find an appropriate q and r. Such a calculation has been performed by D. Harmin and submitted to Physical Review Letters.