at a constant rate of 0.05/nsec. This is generally true in the case where the dissociation yield depends mainly on the laser energy fluence but not on the laser intensity. In fact, the thermal distribution can be approximated only if σ_m in the calculation remains constant or increases slightly with m. We can thus conclude that the thermal distribution is only a rather crude approximation to the laser-excited distribution. Experimentally, this can be verified by an accurate measurement of the dissociation yield, as well as $\langle n \rangle$, versus the laser energy fluence. Recent studies on intramolecular isotope effect in CH_2DCH_2Cl by Colussi, Benson, and Hwang indicated that the excitation energy distribution is indeed narrow.[9] At large dissociation yield, the laser-excited distribution being strongly affected by the fast dissociation will certainly be different from the thermal distribution.

In summary, we have shown that our phenomenological model calculation gives a realistic description of multiphoton excitation and dissociation of polyatomic molecules. Furthermore, it is used to demonstrate that multiphoton laser excitation is not really equivalent to thermal heating.

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Effects of Electric Fields upon Autoionizing States of Sr

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We report the first observation of significant perturbations by external fields of the autoionizing resonance structure of a two-electron atoms. The effects of electric fields up to 20 kV/cm on autoionizing resonances in Sr I were observed by three-photon ionization spectroscopy in an atomic beam. In addition to effects analogous to those for bound Stark states of a one-electron Rydberg atom, we observed a new effect: The characteristic shapes and widths of autoionizing resonances (Fano-Beutler profiles) can be strongly influenced by electric fields.

The occurrence of autoionizing (AI) resonances above the first ionization limit of atomic systems with more than one optically active electron has been the subject of theoretical[1] and experimental[2] investigation for years. Interest in AI states in general, and two-electron AI states in particular, has grown recently with the development of multichannel quantum-defect theory[3] and the experimental techniques of nonlinear sum-frequency generation[4] and multiquantum ionization spectroscopy.[5]

Previously, only the energies and characteris-

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tics shapes of AI resonances have been recorded and assigned.[6] We report here the first observation of significant changes in the shapes and energies of AI resonances in a two-electron atom by controlled external electric fields.[7] We have studied the energy shifts and resonance line-shape variations of AI resonances in Sr between 58 500 and 60 000 cm^{-1} (approximately 14 000 cm^{-1} above the first ionization limit) in fields of 0–20 kV/cm. In this Letter we present detailed measurements of the electric-field behavior of two selected AI states in Sr belonging to $4d(^2D_{3/2})nl$ configurations that clearly demonstrate several remarkable features of the behavior of AI states in electric fields.

For detailed studies of line shapes, we employed three-photon ionization spectroscopy in a collision-free, low-density (~ $10^9/cm^3$) atomic beam.[8] The Sr atomic beam was irradiated between electric-field plates by two laser beams (ω_1 and ω_2) derived from Hänsch-type, pulsed (7-nsec duration) lasers. Both lasers were linearly polarized along the electric-field direction and were focused to a power density of approximately 5 MW/cm^2. One laser frequency was constrained such that $2\omega_1 = 38\,444.1$ cm^{-1}, the energy of the $5s^2 \rightarrow 5s7s$ two-photon transition of Sr I; ω_2 was swept between 20 000 and 21 740 cm^{-1} and the resulting ions produced in the autoionization process were collected and the signal was amplified by an electron multiplier (RCA No. C31019B), and processed by a box-car integrator.

Care was taken to insure that the collection and amplification of the ions were done in a linear fashion. The atomic beam of Sr was sufficiently collimated that the interaction region was well defined, and the electromagnet was operated in a low-gain configuration to avoid any current saturation. The signal was observed to be linear with the intensity of the laser at ω_2.

The $5s7s$ level was chosen as the two-photon resonant intermediate state because of its known strong mixing with doubly excited configurations.[9] We found that excitation of AI levels to be several orders of magnitude more efficient through this level than any other optically accessible two-photon level in Sr I.[10]

The $5s7s$ level is an even-parity, $J=0$ level; in zero electric field, only $J=1$, odd-parity AI states are observed. However, in the presence of a static electric field, the AI Stark states have mixed parity and angular momentum; the transition moment from the $5s7s$ intermediate state to the AI Stark states will in general become field

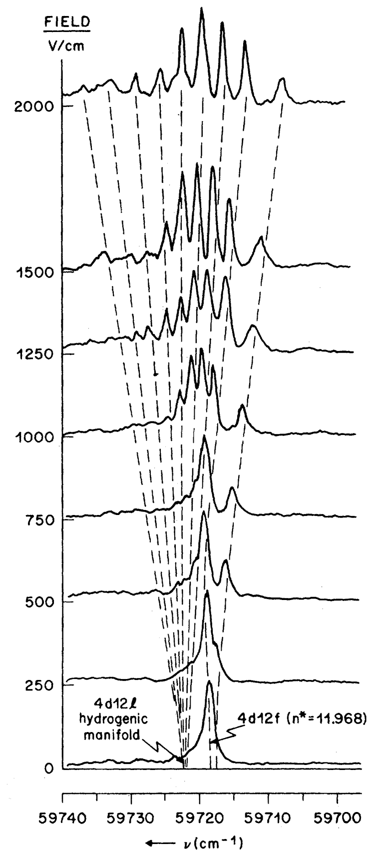

FIG. 1. The electric-field behavior of the $4d12f$, $m=0$ autoionizing resonance in Sr I. In this figure, as well as in Fig. 2, the heights of the signals have been normalized for each separate field value, however, the relative resonance strengths and line shapes for each value are accurate. In both figures the dashed lines are plotted to pass through the observed resonance energies on the abscissa for each field. The resolution of the data is approximately 0.5 cm^{-1}. The $n = 12$ hydrogenlike manifold becomes allowed in the presence of the electric field due to Stark mixing with the $4d12f$ state. Only seven of the eight states in the manifold with $l > 3$ are indicated: The highest-energy Stark state has insufficient admixture of the $4d12f$ state to be visible on this scale. The lowest-energy Stark state in this figure probably connects to a $4d13d$ even-parity state at zero field with a quantum defect of 1.04.

dependent. In Fig. 1, only the $4d12f$ AI state is observable at zero field; with increasing field another AI state (which we have tentatively identified as a $4d13d$ state) is seen to split off to lower energies while for still higher fields the $n=12$ hydrogenlike manifold of high-l states becomes visible. These states have zero-field configurations of $4d12l$, with $l = 3, 4, \ldots, 11$, and become accessible through Stark mixing with the $4d12f$

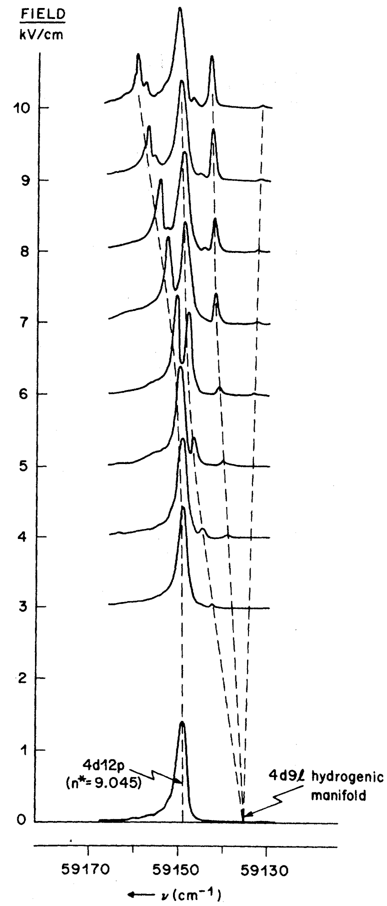

FIG. 2. The electric-field behavior of the $4d12p$, $m = 0$ autoionizing resonance in Sr I. The quantum defect of the $4d12p$ state is nearly 3; thus in the presence of the electric field the higher-lying Stark states of the $n = 9$ hydrogenlike high-l manifold become allowed by mixing with the $4d12p$ state. Only the three highest-energy Stark states of the manifold have sufficient admixture of the $4d12p$ state to be visible. A sharp avoided crossing between a narrow resonance of the $n = 9$ manifold and the wide resonance of the $4d12p$ at approximately 6 kV/cm gives rise to a dramatic change in the resonance profiles. The small resonance structure observable at fields greater than 8 kV/cm probably arises from $m = 1$ states due to impure laser polarization.

level. Because the Stark shift of the resonant $5s7s$ state is negligible for fields used in this study, the extrapolated linear shifts of the manifold to zero field (dashed lines) allows a highly accurate determination of the quantum defect of the $4d12f$ state, $\delta = 0.032$, in agreement with a value determined from linear absorption experiments.[11] In Fig. 2 one observed similar behavior: At zero field, only the $5s7s \rightarrow 4d12p$ transition is allowed; for sufficiently large values of the field, some of the states of the $n = 9$ manifold become observable due to Stark mixing with the $4d12p$ state. Again, an extrapolation of the linear Stark shift to zero field yields a quantum defect for the $4d12p$ state of 2.955.

The shifts of the Stark components are in complete agreement with hydrogenic theory for the equivalent bound levels of the same principal quantum number n.[12] Evidently computational techniques similar to those employed to describe alkali-atom bound Stark states[13] could be used in this case also, *provided* all the relevant zero-field states (even and odd parity) can be identified. However, unlike the previous Stark-effect measurements on bound states,[13] in Figs. 1 and 2 the relative heights of the recorded resonances at each field accurately reflect the relative transition moments. Thus the challenge represented by this data to calculational techniques of Stark effects is considerably more severe.

A closer examination of the data on Figs. 1 and 2 reveals an effect that is peculiar to the Stark effect of AI states and to our knowledge has not been previously observed: The resonance widths and shapes of the AI resonances are clearly seen to be dependent upon the value of the external field, especially at avoided energy-level crossings. (Note the details on Fig. 2 of the avoided crossing between the wide $4d12p$ state and the narrow Stark-manifold state at approximately 6 kV/cm.)

A qualitative understanding of these line-shape changes can be derived from the following simple model. In the state $4dnl$, for $n \gg 4$, the Sr atom may be approximated as a one-electron Rydberg atom with an "excited core," i.e., the second electron is $4d$ instead of $5s$. Autoionization of the $4dnl$ state to a $5s\epsilon l$ continuum state can occur only to the extent that the nl Rydberg electron penetrates the physical region of the $4d$ "excited core." Since this penetration scales as n^{-3}, the AI widths of a nl series should decrease approximately as n^{-3},[14] an observation widely noted in AI spectra.[15] However, because of the angular-momentum centrifugal-potential barrier, penetration also decreases rapidly with l; indeed, it is just this effect that produces the hydrogenlike near-degeneracy in energy for the high-angular-momentum states of a Rydberg atom.[16] Thus states of the $4dnl$ configurations in Sr, with $n \gg 4$, $l > 2$, will become narrower with increasing l.[17]

In the presence of the electric field, the (approximately) stationary Rydberg Stark states will have equivalent penetrations of the excited core region given by the field-induced admixture of the various angular-momentum states. When an avoided crossing occurs between a wide resonance and narrow ones in Fig. 1, the effect on the resulting widths can be thought of in a perturbative sense: To the degree that an otherwise-forbidden high-l-manifold state becomes allowed by an electric-field admixture of an allowed low-l state (e.g., the $4d12f$ level), it necessarily shares the original width of the zero-field low-l state to the same extent. If the avoided crossing is sharp, as in Fig. 2, the effect in the region of the avoided crossing is best analyzed as a level "quenching" phenomenon involving totally mixed wave functions.[18] Assuming an infinitely narrow linewidth for the high-l state at zero field, a symmetric linewidth of 2.7 cm^{-1} for the $4d12p$ state at zero field and a laser resolution of 0.5 cm^{-1}, we have calculated linewidth values in the vicinity of the level crossing at 6 kV/cm in good agreement with the experimental linewidth of approximately 1.2 cm^{-1}.

The approximation inherent in this model can be brought into sharp focus by writing down the wave function of the AI state explicitly[1]:

$$\Psi_{AI}(E) = a(E)\Phi_D + \int b_{E'}(E)\Psi_{E'}dE', \qquad (1)$$

where Ψ_{AI} at energy E is a linear superposition of the bound, discrete state at energy E, Φ_D, and the unbound, continuous eigenvalue state at energy E, Ψ_E. Our model asserts that variations in the line shape of transitions from a bound state to Ψ_{AI} (Fano-Beutler profiles) occur primarily through modification by the electric field of the *discrete part* of Ψ_{AI}. Our data support this conclusion for the states and field strengths used in this study. Although further modeling of this phenomena in terms of the Fano q parameters[1] is now in progress, we hope that this work, and obvious experimental extensions, will stimulate detailed calculations of the Stark effect in quantum systems with interacting bound and continuum configurations.

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