as photoionization measurements are usually carried out under conditions which lead to severe averaging over upper-state excitation energy.

One way to reconcile both types of measurement would be to assume that the predissociation mechanism depends strongly on the excited-state vibrational-mode symmetry. Our results suggest that levels with vibrational energy in a stretching mode dissociate preferentially via ejection of the terminal atom. Study of bending vibrational levels at high optical resolution is definitely necessary in order to establish whether or not they suffer from predissociation with central-atom ejection, a likely interpretation of the photoionization data.

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Resonance in Singlet-Triplet Mixing in Two-Electron Systems Caused by Perturbing Configurations

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The hyperfine structure of the $6snd\,^1D_2$ $(10 \leq n \leq 50)$ Rydberg states of barium has been measured and analyzed in terms of singlet-triplet mixing. A dispersionlike resonant behavior of the mixing coefficient Ω was observed for barium and strontium in the vicinity of doubly excited configurations. In barium strong disagreement with multichannel-quantum-defect-theory wave functions was found. The present results are compared with the spin polarization and anisotropy of photoelectrons.

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Multichannel quantum defect theory[1] (MQDT) is a powerful tool to describe the electronic structure of atomic states simultaneously in the discrete and the continuous parts of the spectrum. Specifically, the wave functions of continuum states of an electron-ion system are closely related to those of the bound states. In order to obtain information about the atomic wave functions the total photoionization cross section and the spin polarization of emitted photoelectrons[2] are equally suited for the determination of lifetimes of Rydberg states,[3] their electronic g factors,[4] Stark shifts,[5] and even isotope shifts.[6] However, such properties of Rydberg states are insensitive to the relative phases of the mixing coefficients in the wave function and only allow the amount of admixture of different configurations to be determined. Similar to the spin polarization of photoelectrons,[7] the hyperfine structure of Rydberg states contains both the magnitude and the relative sign of the admixture coefficient. In this Letter we report the hyperfine splitting of $6snd\,^1D_2$ Rydberg states of barium. Singlet-triplet mixing coefficients Ω are derived and compared with existing MQDT wave functions.[8] Sharp disagreement between experimental and theoretical amplitudes is observed. On the other hand, for strontium we found that MQDT wave functions[9] are consistent with published hyperfine splitting data.[10] To our knowledge, this is the first time that the hyperfine structure of Rydberg states has been exploited to check the relative phases of existing

MQDT wave functions.

For Sr and Ba the singlet-triplet mixing parameter $\Omega(n)$ shows a dispersionlike resonance in the vicinity of doubly excited perturbing states. This resonance has been observed experimentally for the first time. It can be related to the dispersionlike resonant behavior of the asymmetry and spin-polarization parameters[7] of photoelectrons observed recently in mercury when the energy was scanned across certain autoionizing states. Hence, our measurements represent a link between the discrete and continuous parts of the spectrum of two-electron atoms.

Previously, Liao *et al.*[11] have used the hyperfine structure of the $1s3d\,^{1,3}D_2$ states of ^{3}He to derive the sign of the singlet-triplet mixing coefficient, confirming the theoretical result obtained by hydrogenic wave functions. The hyperfine structures of Rydberg states of two-electron atoms such as Yb (Ref. 12) and Sr (Ref. 10) have been reported recently. Although from the measured hyperfine splitting constants of Sr the amount of admixture of singlet into triplet states was deduced[10] and found to agree with theoretical results,[9] no phase information was derived to check the corresponding MQDT wave functions.

Optical-optical double resonance[13] was employed to obtain Doppler-free spectra of $6snd\,^1D_2$ Rydberg states of Ba. They were populated by stepwise excitation from the ground state using two cw dye lasers. Both laser beams counterpropagated through a Ba vapor cell heated to about 480 °C. The first laser beam was tuned to the resonance line at $\lambda_1 = 553.7$ nm while the second laser was scanned across the upper transition $6s6p\,^1P_1 \rightarrow 6snd\,^1D_2$. Spectra were recorded monitoring the transmission of the first laser beam. A marker cavity provided the necessary frequency calibration. Typically an experimental accuracy of ±20 MHz was achieved. Because of optical pumping the technique employed here is very sensitive. On favorable conditions Doppler-free signals were seen with the naked eye.[13] In Fig. 1(a) the positions of the hyperfine components F_f of the final $(6snd\,^1D_2)$ states are plotted as a function of n for ^{137}Ba $(I=\frac{3}{2})$. The frequencies have been measured versus ^{138}Ba. Figure 1(a) clearly exhibits the influence of perturbing states[8] at $n = 14$ $(5d7d\,^3F_2)$ and $n = 26-27$ $(5d7d\,^1D_2)$. The latter one causes the hyperfine splitting factor $A(^1D_2)$ to change its sign between $n = 26$ and $n = 27$, as can be seen in Fig. 1(b).

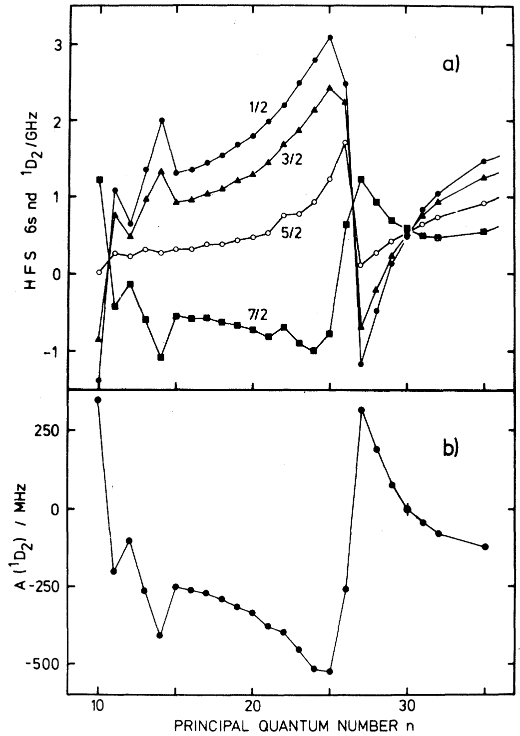

FIG. 1. (a) Hyperfine components F_f of ^{137}Ba, relative to ^{138}Ba, for the $6snd\,^1D_2$ series. (b) Hyperfine splitting factor $A(^1D_2)$ of ^{137}Ba.

In the following we are concerned with the interaction between the $5d7d\,^1D_2$ perturber and the $6snd\,^1D_2$ Rydberg series above $n = 14$. Because of spin-orbit interactions the wave functions of the $6snd\,^1D_2$ and ${}^3D_2$ states in Ba are not exactly LS coupled. For our purposes the wave function $|6snd\,^1D_2\rangle$ can be written as

$$|^1D_2\rangle = \Lambda(^1D_2)\,|^1\overline{D}_2\rangle + \Omega(^1D_2)\,|^3\overline{D}_2\rangle, \qquad (1)$$

where $|^1\overline{D}_2\rangle$ and $|^3\overline{D}_2\rangle$ correspond to the intermediate, exactly LS coupled basis $\bar{\alpha}$ conventionally used in MQDT analyses.[8,9] It is well known from MQDT[8] and lifetime measurements[3,5] that for $15 \leq n \leq 26$ the $^1D_2$ states are of pure $6snd$ configuration, whereas $5d7d$ perturbing configurations $|5d7d\,^1\overline{D}_2, {}^3\overline{D}_2, {}^3\overline{F}_2, {}^3\overline{P}_2\rangle$ are contained in the wave function above $n = 26$. Because of the small core polarization of the $5d7d$ configuration, however, these contributions have been neglected in Eq. (1) since they do not contribute directly to the observed hyperfine splittings. From the spectra of perturbers in the $5d7d$ configuration, we estimate the hyperfine interaction of a pure $5d7d$ state to be of the order of 1% of that of a $6s$ electron. The admixture of perturbers into the $6snd\,^1D_2$ states influences the hyperfine splitting constants [cf. Eq. (2)] indirectly, however, since in that case $\Lambda < +(1-\Omega^2)^{1/2}$. This has been taken into account in the numerical analysis described below. An expression analogous to Eq. (1) holds for $6snd\,^3D_2$ states. As usual, the character of a state is labeled $|^1D_2\rangle$ ($|^3D_2\rangle$) whenever Λ^2 is larger (smaller) than Ω^2. The absolute phases of the wave functions are arbitrarily chosen in such a way that the largest admixture coefficient always enters with a positive sign.

In order to extract $\Omega(^1D_2)$ from the recorded spectra, the hyperfine splitting needs to be calculated. Compared with the strong hyperfine interaction of the 6*s* electron, the contribution of the outer *nd* electron can be neglected. For the hyperfine splitting constant a_{6s} the free-ion value $a_{6s}(137) = 4.016$ GHz can be used to a good approximation. The hyperfine interaction of the 6*s* electron leads to an additional, hyperfine-induced mixing of the $^1D_2$ state with the lower-lying $^3D_{1,2,3}$ fine-structure components. Therefore the wave functions of the odd isotopes differ from Eq. (1) which applies to the even isotopes only. Since we know the hyperfine part of the Hamiltonian exactly within the accuracy demanded by our experiment, the modifications in the wave functions of the odd isotopes can be taken into account quantitatively. For this purpose the Hamiltonian is set up for each *n* within the fine-structure multiplet of the 6*snd* configuration, using the wave functions $|^1D_2\rangle$ and $|^3D_{1,2,3}\rangle$ of the even isotopes as the basis. For these isotopes the Hamiltonian is diagonal with experimental term values appearing as matrix elements. Since the total angular momentum is a rigorous quantum number, for the odd isotopes the matrix can be set up for each value of *F* separately. The positions of the hyperfine components are obtained by diagonalization and adjusted to the experimentally observed ones by a least-squares fit, with $\Omega(^1D_2)$ being the essential fitting parameter. Since the singlet-triplet separation is still fairly large compared with a_{6s}, the exact composition of the $|^3D_{1,2,3}\rangle$ state vectors plays only a lesser role. With neglect of off-diagonal elements, i.e., the hyperfine-induced singlet-triplet mixing, the splitting factor $A(^1D_2)$ can be expressed as

$$A(^1D_2) = a_{6s}[\Omega^2(^1D_2) - 2\sqrt{6}\Lambda(^1D_2)\Omega(^1D_2)]/12. \qquad (2)$$

For sufficiently large singlet-triplet separation, Eq. (2) may be used to derive $\Omega(^1D_2)$. For $^1D_2$ states with some $5d7d$ admixture, the total perturber fraction has to be known. It was taken from either isotope shift data[6] or lifetime measurements.[5] The second term in Eq. (2) immediately reveals that $A(^1D_2)$ depends on the sign of Ω.

In Fig. 2 the experimental singlet-triplet mixing parameter of Ba is plotted as a function of *n*. The most prominent feature is the dispersionlike resonant behavior in the neighborhood of the $5d7d\,^1D_2$ perturbing state, located between $n=26$ and 27. Starting from $\Omega=+0.2$ at $n=15$, the mixing parameter increases regularly up to $+0.54$ at $n=25$. This corresponds to a rotation of the $|^1D_2\rangle$ vector toward the *jj*-coupled basis state $|6snd_{5/2}J=2\rangle$. Between $n=25$ and 27 a rapid drop in Ω to negative values occurs, i.e., the sense of rotation is reversed and the $|^1D_2\rangle$ state vector approaches the $-|6snd_{3/2}J=2\rangle$ function. Above $n=27$, the vector $|^1D_2\rangle$ turns again toward the $|6snd_{5/2}J=2\rangle$ basis vector with increasing *n*. As can be seen from Fig. 2, the state $|6s30d\,^1D_2\rangle$ is exactly *LS* coupled, since $\Omega=0$.

For the barium $6snd\,^1D_2$ series, the MQDT wave functions were calculated by using the eigenquantum defects and unitary matrix $U_{i\alpha}$ reported by Aymar and Robaux.[8] This allows a comparison between experimental and theoretical mixing parameters Ω (Fig. 2). It should be noticed that the absolute phases of the MQDT wave functions have been chosen to comply with the definition given above. As can be seen from Fig. 2, strong disagreement between experiment and theory was found. In particular, the MQDT predicts a pure *LS*-coupled state for $n=23$ with almost zero hyper-

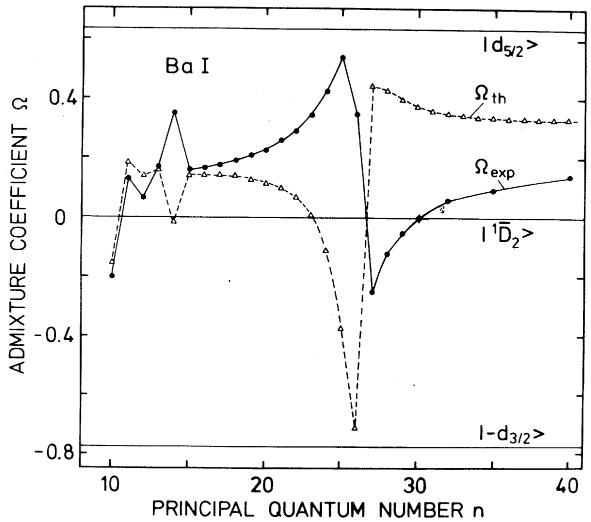

FIG. 2. Experimental and theoretical singlet-triplet mixing parameters $\Omega(n)$ for barium. The size of the experimental data points (dots) corresponds to the error limits of the experimental splitting factor $A(^1D_2)$ of ^{137}Ba.

fine splitting. This is not verified experimentally (Fig. 1). Conversely, the zero hyperfine splitting at $n=30$ contradicts the theoretical value $\Omega_{\text{th}}(n=30)=+0.36$. However, experimental and theoretical mixing parameters agree well between $n=10$ and 13. Furthermore, the twofold crossing of the $\Omega=0$ line above $n=15$ is reproduced by the theory, albeit at energies different from those observed experimentally.

The dispersionlike resonant behavior of the mixing coefficient Ω and the hyperfine splitting factor A is not restricted to barium but occurs for strontium as well. It is known from the MQDT analysis of the $5snd\,^{1,3}D_2$ series[9] that the doubly excited configuration $4d6s\,^{1,3}D_2$ causes a strong singlet-triplet mixing around $n=15$. With the eigenquantum defects and the transformation matrix $U_{i\alpha}$ published by Esherick[9] we have calculated the corresponding MQDT wave functions. We found that the sign of Ω_{th} is consistent with the published[10] hyperfine splitting factors $A(^1D_2)$ and $A(^3D_2)$. In Sr the sense of rotation of the state vector $|5snd\,^1D_2\rangle$ is opposite to that observed for the state vector $|6snd\,^1D_2\rangle$ in Ba when passing through resonance.

In summary, the resonant behavior of the singlet-triplet mixing parameter Ω at perturbing states is a general feature expected to occur, apart from Sr and Ba, for other two-electron systems as well. It represents spin-flip processes induced by doubly excited configurations. The shape of the resonance $\Omega(n)$ will depend on the specific character of the perturbing states. The observed resonances can be compared to the rapid variations of the asymmetry and spin-polarization parameter occurring in photoionization at certain autoionizing states.[7] Common to all these quantities is the phase information about the corresponding wave functions. We conclude from the discrepancy between the experimental and the calculated singlet-triplet mixing observed in Ba that term values alone might be a too-limited data set to determine the relative phases of the $U_{i\alpha}$ scattering matrix.

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