PHYSICAL REVIEW A VOLUME 25, NUMBER 4 APRIL 1982

Systematic investigation of electron densities at the nucleus for Rydberg states of barium

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(Received 5 October 1981)

Isotope shifts of even Ba isotopes in transitions to $6sns\,^1S_0$ and $6snd\,^{1,3}D_2$ Rydberg states have been used to study systematically the change in electron density at the nucleus. For $n \geqslant 11$ the total charge density at the origin approaches that of Ba^+. Local perturbers strongly effect the electron density, and admixture coefficients can be derived which are in quantitative agreement with those from multichannel quantum defect theory.

In medium-heavy and heavy elements the volume shift (VS) is known to contribute a large fraction to the total isotope shift (IS) in optical transitions. Since the VS is proportional to the change in electron density at the nucleus, IS measurments can be used to systematically investigate the saturation behavior of $|\psi(0)|^2$ within a Rydberg series. In particular, for atoms with two valence electrons it is of interest to study the influence of perturber states belonging to a different Rydberg series.

IS measurements involving high Rydberg states have previously been carried out for potassium,[1] rubidium,[2] and for the two-electron systems strontium[3] and ytterbium.[4] In the first three cases the VS is negligible and was not discussed. For Yb the VS remains constant in $4f^{14}6s6p$ - $4f^{14}6snd$ transitions for $n \geqslant 24$. In alkalis the paucity of stable isotopes inhibits investigations of the electronic charge density by means of the volume shift. In alkaline-earth elements the isotopic abundance is more favorable. In particular, barium combines the advantage of a large VS[5,6] with a favorable isotopic composition. In this Communication we report IS results for the transitions $6s6p\,^1P_1 \rightarrow 6sns\,^1S_0$ and $6snd\,^{1,3}D_2$ for the Ba isotopes 134, 136, and 138. For these three series the change in electron density at the nucleus is found to saturate for $n \geqslant 11$. In addition, it exhibits a strongly localized admixture of the $5d7d\,^3P_0$ and $^3F_2$ perturber states into these Rydberg series.

A two-step excitation scheme (Fig. 1) was employed in order to populate the $6sns$ and $6snd$ Rydberg states of Ba around 41 000 cm^{-1}. With the use of two tunable cw dye lasers Doppler-free spectra were obtained, resulting from absorption line narrowing.[7,8] The first dye laser, being resonant with the $6s^2\,^1S_0 \rightarrow 6s6p\,^1P_1$ transition, was kept fixed at 553.7 nm while the second one, operating between 423 and 470 nm, was scanned across the atomic transitions $6s6p\,^1P_1 \rightarrow 6sns\,^1S_0$ and $6snd\,^{1,3}D_2$. Both laser beams were linearly and parallel polarized, and counterpropagating in order to reduce the linewidths of the recorded signals and to achieve optimum resolution. Typical power densities used to excite the first and second transition were 0.3 and 1.5 mW/mm^2, respectively. Spectra were recorded by monitoring the transmission of the green laser beam through the Ba vapor, contained in a heat pipe at about 480 °C and filled with Ar buffer gas at a pressure of 4 mTorr. A marker cavity with free spectral range of 75 MHz provided the necessary frequency calibration.

In Fig. 2 typical spectra of the even Ba isotopes 134–138 are displayed. The upper two spectra correspond to unperturbed members of the Rydberg series, while the lower ones involve perturbed states. As can be seen from Figs. 2(a) and 2(c), virtually the same IS's are observed for the transitions to the un-

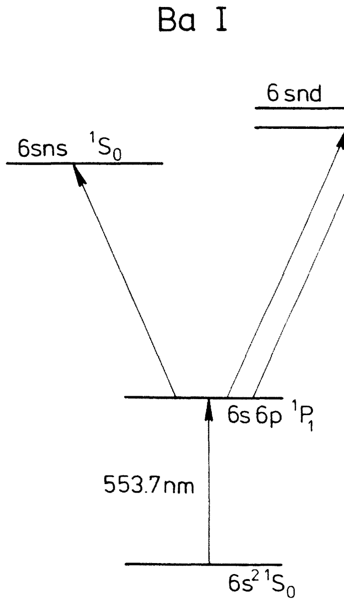

FIG. 1. Atomic levels of barium involved in the two-step excitation scheme.

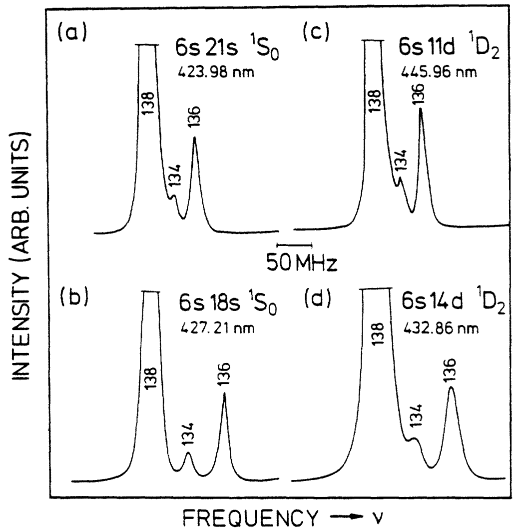

FIG. 2. Doppler-free spectra of the even Ba isotopes 134 to 138 for the transition $6s6p\ ^1P_1 \rightarrow 6sns\ ^1S_0$ [(a) and (b)] and $6snd\ ^1D_2$ [(c) and (d)]. The upper two spectra display unperturbed, the lower ones perturbed members of the corresponding Rydberg series.

perturbed Rydberg states $6s21s\ ^1S_0$ and $6s11d\ ^1D_2$. Indeed, the same holds true for all measured unperturbed members of the $6sns$ and $6snd\ ^1D_2$, $^3D_2$ Rydberg series above $n = 11$. On the other hand, a comparison between the upper and lower spectra shows a conspicuously different IS for transitions to the perturbed states $6s18s\ ^1S_0$ and $6s14d\ ^1D_2$.

The experimentally observed IS (cf. Fig. 2) comprises the individual shifts of both transitions of the cascades. This is a general feature of the absorption-line-narrowing technique[7,8] employed here. Since the IS's of the resonance transition of Ba I at 553.7 nm have been measured with high precision,[5,6] the IS's of the upper transition can easily be deduced.

In order to extract the change in total charge density at the nucleus we compare in a King diagram[9] the IS's of the $6s6p\ ^1P_1 \rightarrow 6sns\ ^1S_0$ (or $6snd\ ^{1,3}D_2$) transitions with those observed for the resonance transition $6s\ ^2S_{1/2} \rightarrow 6p\ ^2P_{1/2}$ of Ba II.[10] We have chosen this transition as reference since the total charge density at $r = 0$ has been calculated by Wilson[11] for the $6s$, $6p$, and $5d$ configurations in Ba^+ using relativistic Hartree-Fock (HF) wave functions. Furthermore, for an alkalilike $6s \rightarrow 6p$ transition, the change in total charge density can be estimated semiempirically.[9,12] In a King diagram a separation of mass and volume shifts is achieved. It results in straight lines connecting different pairs of isotopes. The slope is given by the ratio of the changes in charge density for both transitions; the intersection on the other hand depends on the mass shifts. As an example, the King lines for transitions to $6sns\ ^1S_0$ Rydberg states are shown in Fig. 3. While the intersection of the perturbed state carries interesting information about the specific mass shift, in this Communication we are only concerned with the gradients.

The slopes in the King diagram (Fig. 3) reveal the variation of the change in electron density,

$$|\psi_{6sns}(0)|^2 - |\psi_{6s6p}(0)|^2 ,$$

with principal quantum number, normalized to $|\psi_{6p}(0)|^2 - |\psi_{6s}(0)|^2$ in Ba II. From the slopes it is possible to derive absolute values for

$$|\psi_{6sns}(0)|^2 - |\psi_{6s^2}(0)|^2 .$$

For this purpose we use the theoretical value[11] $4\pi\Delta|\psi(0)|^2 = -128a_0^{-3}$ for the $6s \rightarrow 6p$ transition in Ba II, as well as the result $4\pi\Delta|\psi(0)|^2 = -105a_0^{-3}$ for the $6s^2 \rightarrow 6s6p$ transition in Ba I, deduced from IS data of Baird *et al.*[5] and Nowicki *et al.*[6] Figure 4 shows the change in total electron density at the nu-

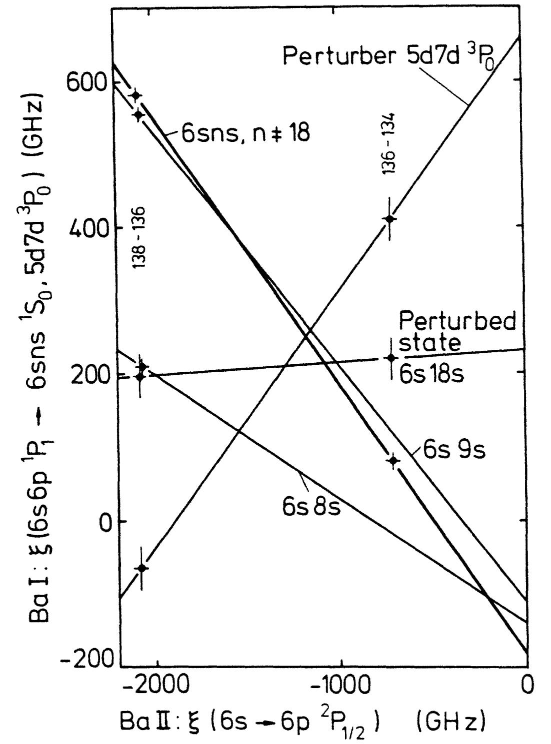

FIG. 3. King diagram relating isotope shifts of the investigated transition in Ba I to the resonance transition in Ba II. The quantity ξ denotes the IS corrected for the normal mass shift and multiplied by the factor $A(A+2)/2$, where A is the mass number. The lines for $6s8s$ and $6s9s$ were calculated from IS data of Jitschin and Meisel (Ref. 16). The heavy line represents the limiting slope, $m = -0.37(5)$, for all pure states $n > 11$.

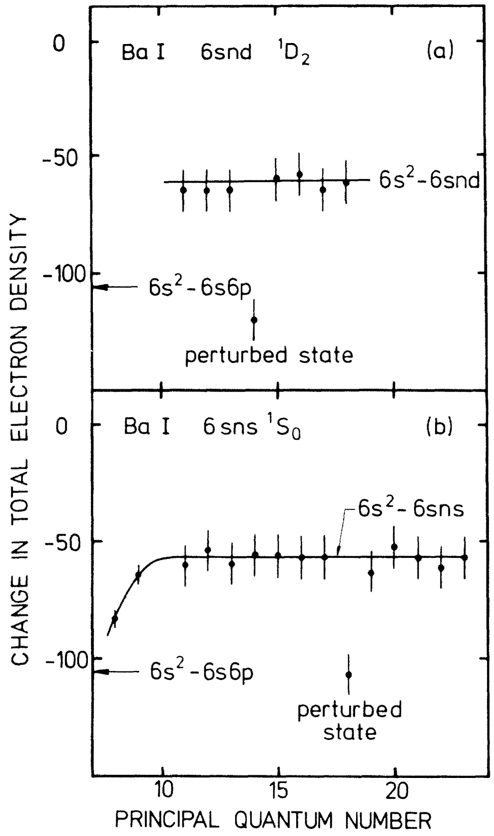

FIG. 4. Change in total charge density at the nucleus, $4\pi\Delta|\psi(0)|^2$ in a.u., between the ground state of Ba I and the Rydberg states investigated. Within our experimental accuracy the saturation limits for the $^1S_0$, $^1D_2$, and $^3D_2$ states are the same. For comparison, the value corresponding to the transition $6s^2 \rightarrow 6s6p$ is indicated. The solid lines are to guide the eye.

cleus between the ground state and the respective Rydberg states as a function of n. Two main features are observed: (i) The saturation value corresponding to the ground state of Ba^+ is reached for $n \geq 11$ and screening effects are dominant only for smaller n; (ii) the drastic deviation of $\Delta|\psi(0)|^2$ for the perturbed Rydberg states $6s18s\,^1S_0$ and $6s14d\,^1D_2$ clearly demonstrates that the admixture of the $5d7d$ configuration is strongly localized.

The saturation limit

$$4\pi[|\psi_{6sns}(0)|^2-|\psi_{6s^2}(0)|^2]=-57(7)a_0^{-3}$$

reached for $n > 11$ represents the change in electron density when ionizing one of the 6s electrons of Ba. This may be compared with the contribution of a single 6s electron in Ba^+ known from hyperfine splitting[13] and relativistic HF calculations[11] to be 105 and $115a_0^{-3}$, respectively. The difference between $110a_0^{-3}$ and $57a_0^{-3}$ shows quantitatively the effect of screening. Such screening effects also occur for excited states $n < 10$ [cf. Fig. 4(b)], and are obviously more important than the density of the ns electron at the nucleus. In this connection it should be noticed that the $6s8s$ and $6s9s\,^1S_0$ states are unperturbed.[14] In Fig. 4 we also indicate the change in total electron density accompanied with the $6s^2 \rightarrow 6s6p$ transition to illustrate the increase in charge density when the $6p$ electron is promoted to the ns or nd orbital.

Next we turn to a discussion of the perturbed states. In Fig. 3 vastly different slopes are found for the $6s18s\,^1S_0$ state as well as for its perturber $5d7d\,^3P_0$ when compared to the unperturbed states $6sns$, $n > 11$. The almost zero gradient for the $6s6p \rightarrow 6s18s$ transition indicates that the increase in charge density expected for a pure state is counterbalanced by the decrease due to the admixture of the doubly excited configuration $5d7d$.[14] Hence, the perturbed state $6s18d\,^1S_0$ has the same charge density at the origin as the $6s6p\,^1P_1$ state, which is also evident from Fig. 4(b). In the following, it will be shown that the observed deviation of the charge density of the perturbed states from the saturation limit can be used to derive the admixture coefficient of the perturber. For this purpose we express the perturbed state as a superposition of pure states corresponding to members of the intermediate LS-coupled channels of Aymar *et al.*[14]

$$|6s18s\,^1S_0\rangle = a|\langle 6s18s\,^1S_0\rangle\rangle + (1-a^2)^{1/2}|\langle 5d7d\,^3P_0\rangle\rangle \quad . \quad (1)$$

When calculating the charge density the interference term

$$\langle\langle 6s18s\,^1S_0\rangle|\delta(\vec{r})|\langle 5d7d\,^3P_0\rangle\rangle$$

vanishes. This is equivalent to the so-called "sharing rule."[15] The charge density of the pure $|\langle 6s18s\,^1S_0\rangle\rangle$ state corresponds to the saturation value [see Fig. 4(b)]. Hence, the first term in Eq. (1) contributes $a^2(-57a_0^{-3})$ to the change in total charge density between the $6s^2$ and $6s18s$ states. The $5d7d$ configuration adds $(1-a^2)(-208a_0^{-3})$. Here we used the average of the upper bound $(-203a_0^{-3})$ derived from IS data[16] for the $6s^2 \rightarrow 5d6d\,^3D_2$ transition, and the lower bound $(-213a_0^{-3})$ calculated[11] for the $5d$ state in Ba^+. Together with the experimentally observed difference of $4\pi\Delta|\psi(0)|^2 = -107(7)a_0^{-3}$ we obtain $a^2=0.67(7)$. This value compares favorably with 0.71 resulting from multichannel quantum defect theory (MQDT) analysis.[14] In a similar manner our isotope shift data for the level $6s14d\,^1D_2$, perturbed by the $5d7d\,^3F_2$ state, show that it is pure to 56%. This too is in excellent agreement with the MQDT result of 57%.[17] Also, for the perturber $5d7d\,^3P_0$, the existing IS data (see Fig. 3) can be analyzed accordingly. This state is found to contain 35% of $|\langle 6s18s\ ^1S_0\rangle\rangle$, again in good agreement with MQDT.

In conclusion, we have demonstrated that the volume shift can be used to infer systematic trends of the electron density at the nucleus for Rydberg states. Medium-heavy and heavy elements are especially suited for this type of investigation. For barium we find a saturation behavior of $\Delta|\psi(0)|^2$ for principal quantum numbers $n \geq 11$, indicating that the total electron density at the origin has reached that of Ba^+. The localized admixture of perturber states can be immediately recognized by a deviating electron density. This can be used to quantitatively derive admixture coefficients. It is expected that IS measurements can be exploited to investigate interchannel mixing between Rydberg series of atoms with two or more valence electrons.

This work was supported by the Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 161. The help of Dr. P. J. West in handling the data is acknowledged.

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