

Isotope-selective photoionization spectroscopy of barium

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We demonstrate an experimental technique that selects the nuclear spin $I=0$ isotope ^{138}Ba for spectroscopic measurements from a beam of natural barium containing seven stable isotopes. A cw dye laser is used to optically pump the $I=\frac{3}{2}$ isotopes ^{135}Ba and ^{137}Ba into the metastable $6s5d\ ^1D_2$ and $^3D_{1,2}$ levels via the $6s6p\ ^1P_1$ excited state, leaving nearly pure ^{138}Ba in the ground state. Photoionization spectra of the excited $5d6p\ ^3D_1$ even isotope state recorded with optical pumping of ^{135}Ba and ^{137}Ba to the metastable levels are essentially devoid of forbidden features associated with the hyperfine interaction in the odd isotopes.

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Resonant multistep laser excitation has played a central role in the study of a diverse range of bound and autoionizing Rydberg-state phenomena. In experimental studies of this type, the symmetry of the final state is selected by the polarization of the lasers used for the multistep process. For two-step resonant excitation from a $J=0$ ground state with linear polarization, selection rules that depend on the angle between the polarization vectors result in final states of $M_J=0$, $J=0$ and 2 or $|M_J|=1$, $J=1$ and 2, respectively, for polarization vectors that are either parallel or perpendicular. These selection rules are based on the assumption that the quantum numbers J and M_J can be treated as constants of the motion. While it is well known that this assumption is not always valid, only recently have experimental and theoretical photoionization studies of the excited Ba $6s6p\ ^1P_1$ and $5d6p\ ^3D_1$ states [1–3] revealed that significant forbidden features appear in the photoionization cross sections. Breakdown of these selection rules on J and M_J is a direct result of the hyperfine interaction in the nuclear spin $I=\frac{3}{2}$ isotopes of barium, ^{135}Ba and ^{137}Ba .

The experimental conditions in Refs. [1,3] were typical of many previous excited-state photoionization experiments in barium that utilized pulsed dye lasers usually pumped by Nd:YAG (neodymium-doped yttrium aluminum garnet) or excimer lasers ([4], and references therein). These pulsed lasers generally have bandwidths of $0.1\text{--}0.5\text{ cm}^{-1}$ (3–15 GHz) and pulse durations of 5–15 ns. The measured hyperfine energy splittings in excited states of the odd Ba isotopes are $\lesssim 800\text{ MHz}$ [5], so the bandwidths of these pulsed dye lasers are too broad to select a single isotope that has no hyperfine structure (e.g., ^{138}Ba with $I=0$). Since the laser pulse duration of $\geq 5\text{ ns}$ is comparable to the hyperfine precession period (i.e., in the vector model picture, the time required for the classical precession of \mathbf{J} about the total angular momentum $\mathbf{F}=\mathbf{I}+\mathbf{J}$), the excited states in the odd Ba isotopes become depolarized, regardless of any time delay between pulses. Depolarization of the excited state leads to forbidden features in the photoionization cross sections. In many instances these forbidden features are easily identified. However, for applications such as Stark spec-

troscopy in the autoionizing region of Ba, where the external field dramatically increases the complexity of the spectrum ([6], and references therein), the forbidden lines can make interpretation of experimental results difficult. More generally, the hyperfine interaction can complicate interpretation of any laser excitation experiment in barium that relies on J and M_J being good quantum numbers. For these reasons, we developed a technique that optically pumps the odd Ba isotopes into the $6s5d\ ^1D_2$ and $^3D_{1,2}$ levels, where they are effectively trapped so that spectroscopic measurements can be performed without the unwanted hyperfine effects. So-called “shelving” [7] of the odd isotopes would be applicable not only to barium but to the alkaline-earth-atom strontium as well. Strontium has only one odd isotope (^{87}Sr , $I=\frac{3}{2}$), but with 7% natural abundance the hyperfine interaction should cause significant breakdown of the selection rules of J and M_J , in the absence of such a shelving process.

There are various experimental techniques that might eliminate the effects of the hyperfine interaction in excited-state photoionization of barium. One obvious solution is to replace natural barium with isotopically pure ^{138}Ba . However, with limited availability and cost exceeding \$1000 per gram, this choice is impractical for a thermal atomic beam apparatus. Separation of the different isotopes by time-of-flight mass spectrometry would solve the problem. However, applications like Stark spectroscopy, where the dc field may be changed frequently, or field ionization, where the electric field is ramped up, could complicate use of the time-of-flight apparatus. Replacing Nd:YAG or excimer-pumped dye lasers with short-pulse mode-locked lasers, for which the pulse duration and delay between pulses are both $\approx 30\text{ ps}$, should preserve the selection rules on J and M_J , but at the cost of a more complicated pulsed laser system. Another method might involve selective excitation of the most abundant $I=0$ isotope ^{138}Ba . For example, excitation of ^{138}Ba to the $6s6p\ ^1P_1$ state at 554 nm looks promising. [The four other even isotopes, $^{130,132,134,136}\text{Ba}$ together comprise only 10.5% of natural barium and do not warrant consideration for selective excitation. Furthermore, the most abundant of these isotopes, ^{136}Ba at

7.9%, is impossible to selectively excite to the $6s6p\ ^1P_1$ state, as it is hidden within the $^{135}\text{Ba}\ 6s6p\ ^1P_1$ ($F = \frac{5}{2}$) line [8].] However, as seen in inset (a) of Fig. 1, with natural linewidths of ~ 20 MHz, the $^{137}\text{Ba}\ 6s6p\ ^1P_1$ ($F = \frac{5}{2}$) hyperfine line and the $^{138}\text{Ba}\ 6s6p\ ^1P_1$ line overlap sufficiently such that unwanted ^{137}Ba would still be excited. In our work, we are primarily interested in spectroscopy of the excited $5d6p\ ^3D_1$ state. Selective excitation of ^{138}Ba may be feasible on the $6s^2\ ^1S_0 \rightarrow 5d6p\ ^3D_1$ transition at 413 nm, since the energy splittings of the $5d6p\ ^3D_1$ hyperfine levels are comparable to those of the $6s6p\ ^1P_1$ levels [5,8], and the linewidths should be narrower for the singlet to triplet transitions. However, to our knowledge the linewidths and isotope shifts for these transitions have not been measured, and since it was sufficiently inconvenient for us to generate stabilized cw laser light at 413 nm, we did not seriously investigate this approach.

Instead, with the above considerations in mind, we took advantage of the fact that the excited $6s6p\ ^1P_1$ state decays to the metastable $6s5d\ ^1D_2$ and $^3D_{1,2}$ levels, allowing the unwanted odd isotopes to be shelved so they cannot participate in the measurements of interest. For the same reason that selective excitation of ^{138}Ba is not feasible on the $6s^2\ ^1S_0 \rightarrow 6s6p\ ^1P_1$ transition, a sizeable fraction of ^{138}Ba is shelved in this process. In addition, since

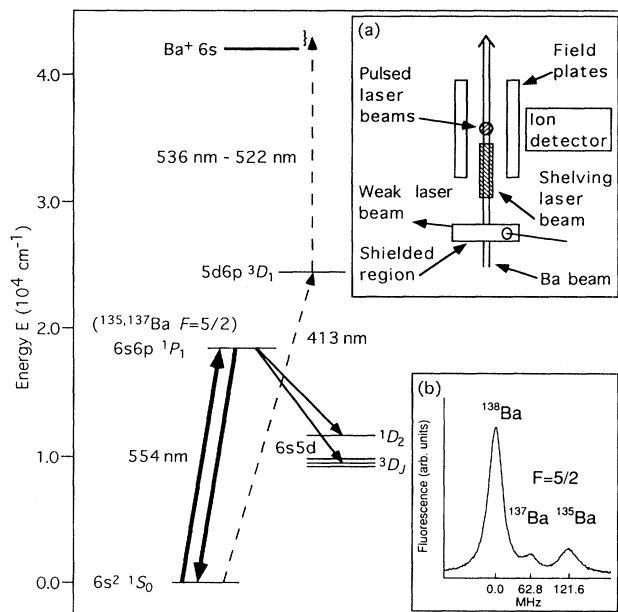


FIG. 1. Energy-level diagram for shelving and photoionization experiments. Bold solid lines indicate the strong ^{135}Ba and $^{137}\text{Ba}\ 6s^2\ ^1S_0$ ($F = \frac{3}{2}$) \leftrightarrow $6s6p\ ^1P_1$ ($F = \frac{5}{2}$) transitions driven by the cw laser. Thin solid lines represent the small branching ratios into the $6s5d\ ^1D_2$ and $^3D_{1,2}$ metastable levels, and the dashed lines represent photoionization of the excited $5d6p\ ^3D_1$ state from the prepared $I = 0$ ground state. Inset (a): diagram of experimental apparatus in vacuum chamber. Inset (b): hyperfine structure of the excited $6s6p\ ^1P_1$ state plotted with respect to the ^{138}Ba line center. The ^{136}Ba line is hidden in the $^{135}\text{Ba}\ F = \frac{5}{2}$ line. The ^{135}Ba and $^{137}\text{Ba}\ F = \frac{3}{2}$ and $F = \frac{1}{2}$ lines lie outside of the plot window.

optical pumping is performed on the ^{135}Ba and $^{137}\text{Ba}\ 6s^2\ ^1S_0$ ($F = \frac{3}{2}$) \leftrightarrow $6s6p\ ^1P_1$ ($F = \frac{5}{2}$) transitions in this work, ^{136}Ba is also shelved. However, this unwanted shelving of some ^{138}Ba and perhaps 100% of ^{136}Ba is not a serious problem with photoionization experiments where ion collection efficiency is high and some loss of signal is acceptable.

In general, shelving requires an atom with an excited state that can be strongly coupled to the ground state, but this excited state must also decay to a lower-lying metastable level. For example, this condition is met for the first excited 1P_1 state in the alkaline-earth atoms calcium, strontium, barium and radium. In barium, the $6s^2\ ^1S_0$ ground state can be strongly coupled to the $6s6p\ ^1P_1$ excited state, which can decay to the metastable $6s5d\ ^1D_2$ and $^3D_{1,2}$ levels with some small probability on each optical cycle. For barium with natural isotopic abundances (^{130}Ba , ^{132}Ba , ^{134}Ba , ^{135}Ba , ^{136}Ba , ^{137}Ba , and ^{138}Ba , respectively, comprise 0.1%, 0.1%, 2.4%, 6.6%, 7.9%, 11.2%, and 71.7%), the measured branching ratios between the $6s6p\ ^1P_1 \rightarrow 6s^2\ ^1S_0$ transition and the $6s6p\ ^1P_1 \rightarrow 6s5d\ ^1D_2$, 3D_2 , and 3D_1 transitions are, respectively, 1/485, 1/1100, and 1/38 000 [9]. Eliminating unwanted hyperfine effects from a beam of barium atoms with the shelving technique is then fairly simple. Output from a stabilized cw dye laser is brought into resonance with the transitions from the ground state to a specific $6s6p\ ^1P_1$ hyperfine level (e.g., $F = \frac{5}{2}$) for each odd isotope. The atoms must be exposed to the laser radiation long enough to allow $\sim 100\%$ of the odd isotopes to decay to the metastable $6s5d\ ^1D_2$ and $^3D_{1,2}$ levels. The spectroscopy of interest is then performed just downstream from the shelving region on a ground state that is essentially pure $I = 0$. This method works well in barium where ^{135}Ba and ^{137}Ba comprise 17.8% of the total isotopic abundance, and it should also work in strontium where ^{87}Sr comprises 7.0% of the total abundance.

Figure 1 shows the experimental method we employ to shelve the two $I = \frac{3}{2}$ isotopes of barium and perform a subsequent photoionization experiment. Inset (a) shows a simple diagram of the apparatus in a vacuum chamber where the lasers interact with a thermal beam of barium atoms with a density of $\lesssim 10^9\ \text{cm}^{-3}$ in a background pressure of $\sim 2 \times 10^{-7}$ torr. The atomic beam has $\lesssim 4$ MHz of residual Doppler broadening when viewed at right angles. Inset (b) in Fig. 1 shows the relevant hyperfine structure of the excited $6s6p\ ^1P_1$ state. As seen in inset (a), the barium beam first passes through a region shielded from stray light where a weak laser beam at 554 nm illuminates the atoms to provide a fluorescence signal for external locking of a stabilized ring dye laser operating on pyromethene 556 dye. The fluorescence signal is coupled out of the chamber to a photomultiplier tube using a fiber bundle. The barium beam then passes between two field plates separated by 1 cm, where the shelving and subsequent photoionization experiments take place. The 554-nm radiation from the ring laser is split into the weak beam and a strong shelving beam, and is locked into resonance with the $^{135}\text{Ba}\ 6s^2\ ^1S_0$ ($F = \frac{3}{2}$) \leftrightarrow $6s6p\ ^1P_1$ ($F = \frac{5}{2}$) transition by externally dither-

ing the laser frequency at ~ 315 Hz and performing phase-sensitive detection on the fluorescence signal from the shielded region. [The intensity of the ^{138}Ba line in inset (b) of Fig. 1 can be suppressed, and the ^{135}Ba and ^{137}Ba lines better resolved, by observing the fluorescence through a linear polarizer [10]. However, unpolarized fluorescence provides an adequate signal for our simple locking scheme.] The strong ring laser beam passes through an acousto-optic modulator (AOM) which shifts 50% of the power in this beam down in frequency by 58.8 MHz to be in resonance with the ^{137}Ba $6s^2^1S_0(F=\frac{3}{2}) \rightleftharpoons 6s6p^1P_1(F=\frac{5}{2})$ transition [8]. The AOM diffracted (frequency shifted) and undiffracted beams are then recombined into a single beam, expanded and collimated, and focused to a line with a cylindrical telescope to overlap the 1-mm-diam barium beam for a length of 2.5 cm to expose the atoms for an average of 60 μs . The total area of the focused line of laser light is ≥ 0.25 cm^2 , and the total combined power is as high as 60 mW (~ 30 mW per isotope), well above saturation intensity for these transitions, which is on the order of 1 mW cm^{-2} .

To perform a measurement free from hyperfine effects, photoionization of the prepared $I=0$ ground state takes place $\lesssim 0.5$ cm downstream from the shelving region. Two Nd:YAG pumped pulsed dye lasers with 5-ns duration pulses and linewidths $\lesssim 0.5$ cm^{-1} excite and photoionize the $5d6p^3D_1$ state. The pulsed laser beams counterpropagate with respect to the shelving beam so that any small deflection of the atom beam due to near-resonant interaction of ^{138}Ba with the cw laser does not require repositioning of the pulsed laser beams. The apparatus for pulsed laser photoionization and collection of Ba^+ has been described in detail elsewhere [3]. The important addition to the experiment here is the stabilized ring laser and associated optics for shelving.

In Fig. 2(a), identical measurements of the photoionization spectrum of the $5d6p^3D_1$ state between 0.095 and 0.166 eV above the Ba^+6s threshold, with and without shelving, and for parallel polarization, are plotted against the ionizing laser wavelength. Figure 2(b) shows identical measurements as in Fig. 2(a) for perpendicular polarization with full scale in (b) identical to (a). In both (a) and (b), the spectra with the shelving beam on have the smaller peak heights and lower baselines, and display a conspicuous absence of forbidden resonances. For the spectra where the shelving beam and weak locking beam were off, arrows denote the strong forbidden resonances. In the parallel measurement of Fig. 2(a), these resonances have $|M_J|=1$ and $J=1$, while in the perpendicular measurement of Fig. 2(b), they have $M_J=0$ and $J=0$. It is quite easy to identify forbidden resonances by comparing the two different final-state symmetries for this portion of the spectrum where the density of states is so low.

Although with shelving to the metastable levels there is a substantial reduction in the Ba^+ signal, this method is very effective for identifying and removing forbidden features from the photoionization spectrum that are present due to the hyperfine interaction in the odd Ba isotopes. Comparison of the baselines for shelving on and off in either Fig. 2(a) or 2(b) reveals that the reduction of

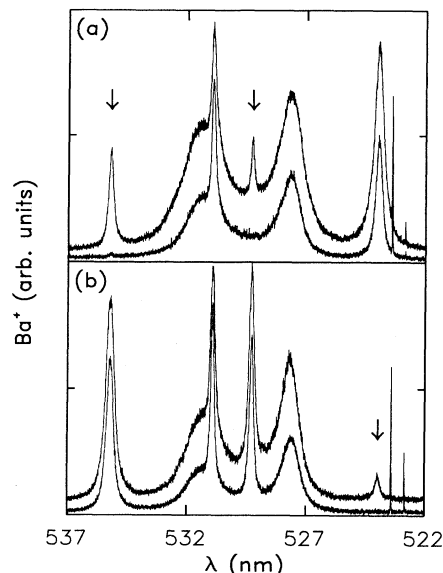


FIG. 2. (a) Identical measurements of the photoionization cross section of the excited $5d6p^3D_1$ state for parallel polarization with and without shelving of ^{135}Ba and ^{137}Ba . Arrows denote the forbidden resonances in the measurement without shelving. (b) Same as in (a) but for perpendicular polarization.

Ba^+ was greater than $\sim 18\%$, as would be expected due to removal of ^{135}Ba and ^{137}Ba alone. This extra reduction resulted primarily through shelving of ^{138}Ba and ^{136}Ba , as discussed earlier. In addition to this extra reduction in Ba^+ , the strength of the forbidden and allowed resonances in (a) and (b) did not always scale according to the abundance of the odd isotopes and the degree of hyperfine depolarization of the excited $5d6p^3D_1$ state as one might expect. For example, the forbidden $J=1$ resonance near 535 nm in the unshelved spectrum of (a) is roughly half the size of the same allowed resonance in the unshelved spectrum in (b). On the other hand, the size of the forbidden $J=0$ resonance near 524 nm in the unshelved spectrum of (b) is roughly 5–10% of the size of the same allowed resonance in the unshelved spectrum in (a). Estimates of the ratios of these peak heights would indicate that both should be close to 5–10% [2,3]. These discrepancies appear to be caused by the phenomenon of depletion broadening [11–13], where the ionizing laser power depletes the excited $5d6p^3D_1$ state population to such an extent that the observed signal (the number of Ba ions produced) saturates and is no longer proportional to the photoionization cross section. A simple estimate of the degree of saturation supports this hypothesis since calculations [3] show that the $J=1$ resonance near 535 nm is at least twice as strong as the $J=0$ resonance and hence more likely to saturate. In addition, the scanning laser power, which varies as the dye efficiency curve, was greater at 535 nm. Each individual spectrum in Fig. 2 was normalized with respect to the ionizing laser power, but this procedure is strictly valid only when the cross section is small and cannot compensate for the effects of depletion broadening at a strong resonance.

In Fig. 3, two more parallel polarization spectra are

plotted against ionizing laser wavelength over a narrower energy range, but now in the presence of an external electric field of 15 kV cm^{-1} . An additional autoionizing resonance appears at 533 nm due to field-induced mixing with states of odd parity, but the forbidden line near 535 nm is still effectively removed by shelving. That shelving works well in external fields is not surprising since there should be no significant reduction in the lifetime of the metastable $6s5d \ ^1D_2$ levels due to field-induced mixing with the $6s6p \ ^1P_1$ levels for laboratory fields.

Careful examination of both Figs. 2 and 3 reveals that a small amount of the forbidden symmetry is still present in these measurements. A likely contribution to the presence of the forbidden symmetry is a small error in the angle between the polarization vectors of the two lasers. A calculation of these cross sections from the methods in Refs. [2,3] reveals that an error in this angle of less than 2° gives rise to small but identifiable forbidden resonances. Another consideration is the Doppler shift of the odd isotopes due to recoil momentum. However, with power broadened linewidths greater than 20 MHz, this shift should not affect the rate of shelving to the metastable levels.

In summary, we have developed and demonstrated a simple experimental technique based on optical pumping that eliminates hyperfine effects from spectroscopic measurements in natural barium. This technique of shelving odd isotopes in metastable levels has broad application to many atoms, but is perhaps best suited to the alkaline-earth atoms barium and strontium. The shelving method can be used for a broad range of experiments since the low-lying metastable levels are generally unaffected by typical laboratory fields. The significance of this tech-

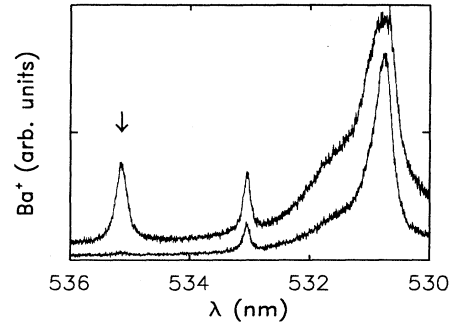


FIG. 3. Identical measurements of the photoionization cross section of the excited $5d6p \ ^3D_1$ state for parallel polarization with and without shelving of ^{135}Ba and ^{137}Ba in an external field of 15 kV cm^{-1} . The arrow denotes the forbidden resonance in the measurement without shelving. The additional resonance at 533 nm is due to field mixing of states with odd parity.

nique derives from interest in the heavy alkaline-earth atoms as systems for the study of two-electron motion. When the shelving method is employed, analysis of experimental results that rely on J and M_J being good quantum numbers can, under many conditions, be greatly simplified.

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