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Photoionization of the Ba $6s6p\ ^1P_1$ state

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In an effort to explain two disagreeing experimental measurements of photoionization cross sections, we employ an eigenchannel R-matrix approach using a jj-coupling basis set to calculate the photoionization of the excited state $6s6p\ ^1P_1$ of barium from threshold to about 3-eV photoelectron energy. The calculated cross section shows rich structure due to the breakdown of the LS coupling and mixing of several Rydberg series. Our results are in approximate agreement with one measurement farther from threshold, but indicate that the absolute normalization of another measurement at and around threshold is in error.

Photoionization cross sections from excited atomic states have recently been the subject of increased experimental attention due to the availability of the necessary tools (lasers), and of increased theoretical attention. The theoretical calculations (and most of the measurements) treat excited states of alkali-metal atoms because of their simplicity and they include Hartree-Slater, Hartree-Fock, multiconfiguration Hartree-Fock, and random-phase approximation calculations. Agreement between theory and experiment for these atoms has reached a generally satisfactory level.

Alkaline-earth atoms have also been studied experimentally and in particular the excited configurations $6s5d$ and $6s6p$ of Ba have been both measured[1-3] and calculated.[1,4] Theory and experiment agree on the $6s5d$ $5d$-photoionization both in the regions where the channel interaction is negligible and where autoionizing states and inner-shell excitation are becoming dominant contributors to the cross section.

The photoionization of $6s6p\ ^1P$ still presents a puzzle, however. A simple Hartree-Slater (HS) calculation by one of the authors[4] predicts smooth behavior with energy (since it does not include any channel coupling). There are two experimental measurements at (slightly) different energies but both close to threshold, and both works claim that their cross-section values are absolute and derived through different approaches. The two measurements, however, quote values differing by a factor of 25. Specifically, Kallenbach, Koch, and Zierer[2] report ~ 600 Mb at 417 nm compared with ~ 20 Mb from Ref. 4 whereas Burkhardt *et al.*[3] measured 17.6 ± 2.3 Mb at photon energies 354.7 nm compared with about 12.5 Mb from Ref. 4.

In this Rapid Communication we use the eigenchannel R-matrix approach, combined with multichannel quantum-defect theory (MQDT) that has been described in detail elsewhere.[5] An added feature of the present calculation is that it used jj-coupling basis functions,[6] rather than the previously used LS-coupling basis. Moreover, the spin-orbit interaction for each electron was included explicitly in the Hamiltonian within the R-matrix box as in Ref. 6. The e-Ba^{2+} interaction was described by a one-electron analytic potential $V(r)$ developed by Aymar.[7]

$$V(r) = -\frac{1}{r}[Z_c + (Z - Z_c)e^{-a_1 r} + a_2 r e^{-a_3 r}] - \frac{\alpha_c}{2r^4}(1 - e^{-(r/r_c)^6}) . \quad (1)$$

Here $Z_c = 2$, $Z = 56$, while the parameters $\{a_1, a_2, a_3, r_c\}$ were adjusted by Aymar[7] to reproduce the one-electron spectrum of Ba^+. The parameter α_c is the known static dipole polarizability of Ba^{2+}. The initial state was described by a 401-state basis whereas the $J = 0$, 1, and 2 final states were described by 200–500 variational basis functions within an R-matrix box of radius $r_0 = 25$ a.u. The types of channels included in the MQDT calculation were $6sns$, $6snd$, $5dns$, $5dnd$, and $6pnp$. Numerous other "strongly-closed-type" basis functions such as $5dng$, $7sns$, etc., were included in the variational basis set within the box. It should be noted that the two-electron model Hamiltonian used here is appropriate for photoionization of the outermost (valence) electrons only.

Our composite results for the processes

$$\mathrm{Ba}(6s6p\ ^1P_1) + h\nu \rightarrow \mathrm{Ba}(6s)^+ + \epsilon l \quad (J = 0,1,2) \quad (2)$$

are shown in Fig. 1. We observe a very rich structure due to strong channel interactions, and partly to the breakdown of the LS-coupling scheme. A point of particular interest is the broad "complex resonance" between 365 and 375 nm which corresponds to the $6p^2\ ^1S^e$ state predicted by Aymar *et al.*[8] to lie above the $6s$ threshold. A parallel calculation by Bartschat and McLaughlin[9] using the Belfast R-matrix code produces results of similar magnitude near threshold and spectra of similar complexity. That work, however, does not exhibit this prominent $6p^2$ feature. This perturbing level has apparently been observed by Aymar, Camus, and El Himdy[10] near $\lambda = 374$ nm, which is slightly lower in energy than our calculated position here.

It is important to provide some explanation of the disagreement between the present calculation and both

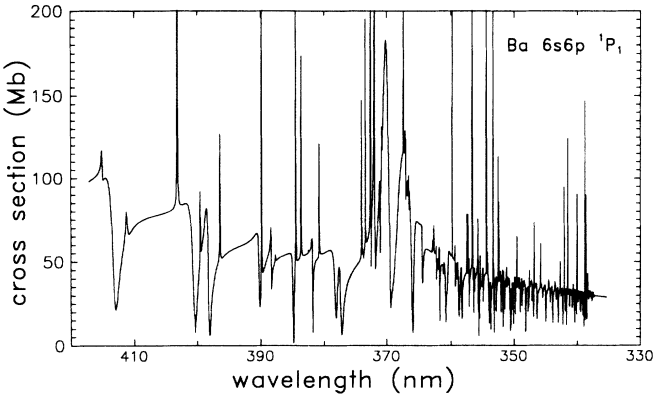

FIG. 1. Total photoionization cross section predicted for the Ba $6s6p\ ^1P_1$ initial state.

the HS values[4] and the measurements of Ref. 2. First, the HS approximation treats the electron-core exchange as a local function of the distance, and as such it is not accurate in determining the wave functions and, especially, the phase shifts near threshold as was shown in detail by Theodosiou and Fielder.[11] Probably more important, though, is the fact that the single-channel HS calculation fails to account for the very critical effects of channel interaction and autoionization. That calculation, however, should give a reasonable representation of the average photoionization cross section away from threshold, as was seen in the case of Ba $6s5d\ 5d$-photoionization.[4]

Our calculated photoionization values in the region of the measurement of Ref. 3 is shown in Fig. 2, where the two results are compared. It is fair to say that the agreement of the present calculation and the measurement of Ref. 3 is satisfactory, considering that the calculation has not been fully optimized yet. We used the experimental value 417.155 nm for the photoionization threshold. At worst, there might be a factor of 2 difference between experiment and theory. Consequently, the claim of Burkhardt *et al.*[3] of being able to obtain absolute cross sections seems to be substantiated. It should be remarked that there is a misprint in Ref. 3, where the photon wavelength should be 3547 Å (the frequency tripled Nd:YAG (where YAG denotes yttrium aluminum garnet) laser beam of 10640 Å] rather than the printed 3533-Å value.[12]

Our results near threshold are shown in Fig. 3 and compared with the measurements from Ref. 2. We see that the general shape of the experimental curve follows the theoretical one, but the experimental data must be divided by roughly 5.5 to bring them to the same scale as the theory. Two resonance features appear in the theoretical $J=2$ cross section in the range of Fig. 3. The first is an asymmetric autoionization profile near $\lambda=415.3$ nm that apparently is the level denoted $5d_{5/2}7d_{5/2}$ by Aymar, Camus and El Himdy.[13] Judging from Fig. 4 of Ref. 13, this level should be expected to lie roughly at 415.7 nm. The second calculated $J=2$ resonance in Fig. 3 is a window resonance near $\lambda=413$ nm. This is apparently the $J=2$ level denoted $5d_{3/2}9s$ by Refs. 13 and 14, which is observed at $\lambda=413.7$ nm but is seen closer to 412 nm in the experiment of Kallenbach *et al.*[2] The lone calculated $J=0$ resonance near $\lambda=411.2$ nm in Fig. 3 must be the level $5d_{5/2}7d_{5/2}$ of Ref. 13. Based on Fig. 2 of this reference, the approximate position is expected to be $\lambda=411.3$ nm.

Note that the two features seen in Ref. 2 are shifted in opposite directions with respect to the theory. Of course, division of the data by a factor, constant at all energies, may not be the most appropriate treatment to overcome such a disagreement in magnitude. For example, we cannot be certain as to what features the possible background contributions have. Nevertheless, unless contributions from other sources, like the presence of dimers, can be eliminated, one may have differences of several orders of magnitude, as was the case, e.g., between the early experiments and theory of the two-photon ionization of Cs.[15] Figure 3 of Ref. 2 apparently has a misprint, as the photoionization threshold there is marked at 416 nm, about 1

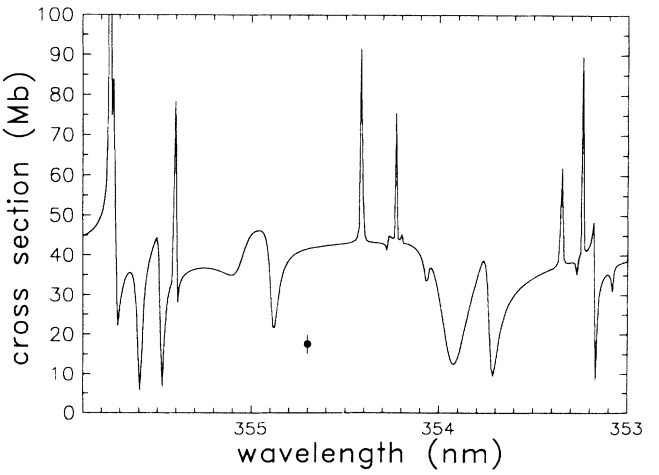

FIG. 2. Total photoionization cross section of the Ba $6s6p\ ^1P_1$ state around 354.7 nm. The experimental point is from Ref. 3.

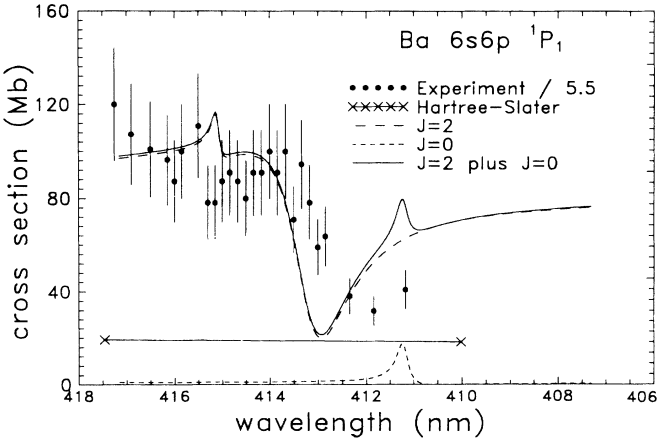

FIG. 3. Total photoionization cross section of the Ba $6s6p\ ^1P_1$ state near the $6p$ threshold. The experimental points are those of Ref. 2, divided by a factor of 5.5. We caution that this rescaling of the Ref. 2 data is tentative and requires further justification.

nm too large. The reduction of the photoionization cross section from the raw data by Kallenbach *et al.*[2] may be seriously flawed by assumptions made there. For example, they use one known transition probability and make a rather drastic scaling assumption. It could very well be that the scaling itself is incorrect or that the single value used is inaccurate. A particularly questionable assumption of this work may be that "all Rydberg states selected have the same branching fraction to the $^1P_1^\circ$ state." Past experience from work with Rydberg states of alkali atoms[16] and spin-allowed transitions in helium[17] indicates that the branching ratios are approximately constant from state to state, but this may not be true here where doubly excited perturbing configurations can have a dominant effect.

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