Microwave spectroscopy of autoionizing Ba $5d_{3/2}n\ell$ states

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We have observed microwave resonance transitions between the autoionizing Ba $5d_{3/2}ng J=2$ and $5d_{3/2}(n + 1)h J=3$ states for $45 \le n \le 49$. These measurements, made between 50 and 75 GHz, lead to quantum defects of +0.019(2) and +0.003(2) for this pair of ng and nh states. These measurements demonstrate that the core polarization model, widely used to characterize nonpenetrating Rydberg states, fails to describe Rydberg states converging to anisotropic or non s cores. In particular, the second order quadrupole interaction cannot, in general, be represented in this manner.

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I. INTRODUCTION

A high *n*, or Rydberg, electron in a high- ℓ state is sensitive primarily to the charge of its ionic core, and the electron can thus be represented very well by hydrogenic wave functions, which have well known properties. Here *n* and ℓ are the principal and orbital angular momentum quantum numbers of the Rydberg electron, and we use atomic units unless indicated otherwise. The small differences of the Rydberg energies from the hydrogenic value of $-1/2n^2$ are due to the differences between the finite sized ionic core and a point charge. Using the well known properties of the hydrogenic wave functions we can relate these small energy shifts to properties of the ionic core. This notion was first realized by Mayer and Mayer who suggested that the field from the slowly moving Rydberg electron polarizes the ionic core, and that for isotropic cores the primary deviation of the Rydberg energy levels from the hydrogenic value is due to core polarization if the Rydberg electron is in a nonpenetrating orbit [1]. Explicitly, the energy of the $n\ell$ level is given by [2]

$$W_{n\ell} = -\frac{1}{2n^2} - \frac{1}{2}\alpha_d \langle r_{n\ell}^{-4} \rangle - \frac{1}{2}\alpha_q \langle r_{n\ell}^{-6} \rangle, \qquad (1)$$

where α_d and α_q are the dipole and quadrupole polarizabilities of the ionic core, and $\langle r_{n\ell}^{-4} \rangle$ and $\langle r_{n\ell}^{-6} \rangle$ are expectation values of inverse powers of the radial coordinate of the Rydberg electron. For Rydberg states converging to the ground state of the ion the polarization shift is always to lower energy, and many accurate determinations of the polarizabilities of alkali ions have been made by using Eq. (1) to fit Rydberg energy level spacings.

Equation (1) is only strictly correct for an isotropic ionic core. If the core has total angular momentum $j \ge 1$ it has a tensor polarizability as well. More important, a $j \ge 1$ core can have an electric quadrupole moment which produces a first order interaction with the Rydberg electron and splits the $n\ell$ level, often leading to states lying above the hydrogenic energy.

Analyses of high- ℓ Rydberg states converging to anisotropic cores have only been done in a few cases. Pruvost *et al.* examined Rydberg states converging to the Ba⁺ 6p_{3/2} and 6d_{5/2} ionic cores. They observed very evident tensor energy splittings which were mostly due to the first order quadrupole and second order dipole interaction between the Rydberg electron and the Ba⁺ core [3]. Chang and Sakai have extracted the quadrupole moments of C⁺, N⁺, and Ne⁺, from energy splittings of the *nf* Rydberg states observed in optical spectra [4]. Ward *et al.* examined the Ne²P_{3/2}10ℓ states, $5 \le \ell \le 8$, using radio frequency resonance spectroscopy and were able to make a precise determination of the Ne⁺²P_{3/2} quadrupole moment [5]. Perhaps most surprising is that it is even possible to extract information regarding the hyperfine structure of the ion from the Rydberg states. This has been done for H₂⁺ by Sturrus *et al.* [6] and Osterwalder *et al.* [7] using optical, radio frequency, and microwave resonance techniques.

With the exception of the work on Ne, no microwave or radio frequency resonance experiments have been done on Rydberg states converging to anisotropic cores. Furthermore, all experimental efforts have been focused on bound Rydberg states, i.e., those converging to the ground state of the ion.

Here we report microwave resonance measurements of Ba $5d_{3/2}ng-5d_{3/2}nh$ intervals. These measurements differ from previous resonance measurements in that these states lie above the lowest ionization limit and autoionize. These measurements present a significant challenge relative to resonance measurements on bound states. The Ba $5d_{3/2}ng$ states we have studied have 5 ns lifetimes due to autoionization, and to observe a signal we must drive the ng-nh transition with a Rabi frequency comparable to the inverse of this lifetime. As a consequence, the required microwave power is a factor of 10⁶ higher than that required to drive an equivalent transition between more typical Rydberg states with a 5 μ s lifetime [8]. In addition, since autoionizing states decay quickly, it is not at all obvious that it will be possible to detect transitions between them, although it apparently is. These measurements represent the first step towards using resonance spectroscopy to probe autoionizing states. While resonance measurements of autoionizing states present a substantial challenge, they may provide a new probe for the properties of the ionic core. Specifically, the first order interaction with degenerate continua leading to autoionization provides a probe of specific ionic matrix elements.

In the following sections we describe our experiment, compare our observations to the results of a simple model



FIG. 1. Energy level diagram showing the laser excitation of the $5d_{3/2}ng J=2$, K=5/2 state (\rightarrow) and the microwave transitions to the $5d_{3/2}(n\pm 1)h J=3$, K=7/2 states (\sim).

calculation, and outline why the adiabatic model for the quadrupole polarizability of Eq. (1) is not particularly useful for anisotropic or non *s* cores.

II. EXPERIMENTAL APPROACH

In the experiment a thermal beam of Ba atoms passes between two plates 4.5 cm apart, where the atoms are excited by two temporally overlapped 5 ns dye laser pulses which are counter propagating to the atomic beam. The atoms are excited from the ground $6s^{2-1}S_0$ state to the 5d6p ${}^{3}D_{1}$ state and then to the $5d_{3/2}ng J=2$ state, as shown in Fig. 1. The laser excitation occurs in the presence of a 50–75 GHz microwave field which drives the $5d_{3/2}ng$ $\rightarrow 5d_{3/2}(n \pm 1)h$ transitions. The microwave field is turned off 100 ns after the laser pulses. To detect the $g \rightarrow h$ transitions we use a delayed field ionization technique [19]. A negative voltage pulse of up to 800 V is applied to the lower plate 1 μ s after the laser pulses to field ionize the $5d_{3/2}n\ell$ atoms and drive the resulting electrons through a hole in the upper plate to a dual microchannel plate detector. The $5d_{3/2}ng$ states of $n \sim 45$ have lifetimes of ~ 5 ns while the $5d_{3/2}nh$ states have lifetimes >300 ns, so only when the microwaves drive the $g \rightarrow h$ transition do we observe a field ionization signal. The $5d_{3/2}ng$ J=2 lifetimes we observe are shorter than expected from an extrapolation of those of lower lying $5d_{3/2}ng J=2$ states [9,10], which may be due to the presence of a perturbing state converging to a higher limit. In this connection we note the presence of the $5d_{5/2}14d$ J=2 states with term energies of 46 853 and 46 874 cm^{-1} (see Ref. [11]). These levels are approximately degenerate with the Ba $5d_{3/2}45g$ and $5d_{3/2}56g$ states, and could be the source of the increased decay rates. Such an interaction was suggested as a possible cause of the increase in the scaled linewidths of the Ba $5d_{3/2}np$ and $5d_{3/2}nf$ series at high n (see Ref. [12]).



FIG. 2. Resonances observed from the $5d_{3/2}49g$ state to the $5d_{3/2}50h$ and $5d_{3/2}48h$ states at 55.142 and 56.829 GHz.

measure its frequency with a HP 5343A counter. The continuous wave 12–19 GHz output of the sweep oscillator is formed into pulses with a General Microwave DM862B switch. To generate the 50–75 GHz microwaves we use a Phase1 SX 40–220 active doubler followed by a HP R382A precision attenuator and a Pacific Millimeter V2 passive doubler, leading to 3 mW of power in the 50–75 GHz range. The power is then transported by WR19 waveguide through a feedthrough to a horn inside the vacuum system. The horn is 5 cm from the atoms.

III. OBSERVATIONS

To record the data we sweep the microwave frequency, over many shots of the laser, while monitoring the field ionization signal. We average repetitive sweeps until we obtain a reasonable signal to noise ratio. As an example, the two resonances observed when starting with the $5d_{3/2}49g$ state, the $5d_{3/2}49g \rightarrow 5d_{3/2}50h$ and $5d_{3/2}49g \rightarrow 5d_{3/2}48h$ resonances, are shown in Fig. 2. To record the resonances shown in Fig. 2 we reduced the microwave field to yield the smallest observable linewidth, which is approximately what can be expected from the $5d_{3/2}ng$ 5 ns lifetime. We assign the resonances as $ng \rightarrow (n \pm 1)h$ by the field required for field ionization of the $(n \pm 1)h$ state. The (n+1)h state requires a lower field than does the (n-1)h state. It is interesting to note that the fields required for the field ionization are essentially the same as those required for ionization of bound states of the same n. On the basis of earlier experiments on autoionization of Ba $6p_{1/2}n\ell$ atoms in static and microwave fields we were initially surprised by this observation [13]. This difference is no doubt due to the fact that $Ba6p_{1/2}n\ell$ states decay by dipole autoionization to $6s_{1/2}\epsilon\ell'$ and $5d_i\epsilon\ell'$, $\ell' = l \pm 1$ continua, while $5d_{3/2}n\ell$ states decay to $6s_{1/2}\epsilon\ell'$, $\ell' = l, \ell \pm 2$ continua by quadrupole autoionization. The quadrupole autoionization rates fall faster with ℓ than do the dipole rates, so the change in lifetime with ℓ is more dramatic in the Rydberg states converging to the $5d_{3/2}$ core than in those converging to the $6p_{1/2}$ core.

The observed frequencies of Table I are fit to the expression

TABLE I. $ng \rightarrow n'h$ frequencies. All transitions are J=2 K = $5/2 \rightarrow J=3$ K=7/2.

n	n'	Frequency (GHz)
49	50	55.142 (9)
	48	56.829(11)
48	49	58.659 (8)
	47	60.471 (6)
47	48	62.433 (8)
	46	64.442(14)
46	47	66.567 (6)
	45	68.794 (6)
45	46	71.030 (8)
	44	73.528(10)

$$\nu = R \left[\left[\frac{1}{(n - \delta_g)^2} - \frac{1}{(n \pm 1 - \delta_h)^2} \right] \right]$$
(2)

to find the average value of the g and h quantum defects over this n range, which leads to $\delta_g = +0.019(2)$ and δ_h = +0.003(2). For Ba we use the value R=3.289 844 ×10¹⁵ Hz. We obtained this value by using R_{∞} corrected by the reduced mass factor.

There is only one observable transition when starting from the $5d_{3/2}ng J=2$ states. These states are best described in *jK* coupling, i.e., the angular momentum, *j*, of the core is coupled to the orbital angular momentum, ℓ , of the Rydberg electron to give *K*, i.e., $\overline{j}+\overline{\ell}=\overline{K}$. The Rydberg electron spin is then added to \overline{K} yielding the total angular momentum \overline{J} , $\overline{K}+\overline{1/2}=\overline{J}$. The $5d_{3/2}ng J=2$ state has K=5/2, and the only electric dipole allowed transition is to the $5d_{3/2}nh J=3$ K=7/2 state. We are able to determine the one *ng-nh* interval shown in Fig. 3.

The only reported values for Ba $5d_{3/2}ng$ quantum defects are those due to Bente and Hogervorst [10]. Using laser



FIG. 3. Schematic diagram of the $5d_{3/2}ng$ and $5d_{3/2}nh$ energy levels showing the observed $K=5/2 \rightarrow K=7/2$ transition. The energy of a hydrogenic $n\ell$ state is shown by the dotted line. The transitions we observe are between the highest lying levels.

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Term Energy (cm⁻¹)

FIG. 4. Quantum defects of the Ba $5d_{3/2}ng J=2 K=5/2$ states observed by Bente and Hogervorst (•). They extrapolate to a value of 0.015(1) at $n \sim 45$, far below our observed quantum defect of 0.019(2)(\blacksquare). We have assigned an uncertainty of 1 GHz, or one tenth of the laser linewidth, to the measurements of Bente and Hogervorst because no uncertainties were given.

spectroscopy they observed the J=2 series and two J=4series for levels of $11 \le n \le 20$ (see Ref. [10]). In Fig. 4 we plot their quantum defects for the Ba $5d_{5/2}ng J=2$ states and ours. As shown, our quantum defects are not consistent with an extrapolation of theirs to $n \approx 50$, which would give $\delta_g = 0.015(1)$, substantially smaller than our value of 0.019(2). We believe that the higher lying Ba $5d_{3/2}ng$ states are depressed in energy by interaction with states converging to the $5d_{5/2}$ limit, probably the $5d_{3/2}14d J=2$ states noted earlier. Such an energy shift would be consistent with the increased autoionization rates of the $5d_{3/2}ng$ states over those expected from an extrapolation the rates of lower lying levels.

Bente and Hogervorst have also observed several 5dng and 5dnh J=4 and 5 states. Most were Rydberg states converging to the $5d_{5/2}$ limit, but they did observe two $5d_{3/2}ng J=4$ Rydberg states, with quantum defects 0.0312 and 0.0294, and two $5d_{3/2}nh J=5$, states, with quantum defects 0.0190 and 0.0117. The ng states should be K=7/2 and 9/2, and the nh states K=9/2 and 11/2. Their quantum defects are consistent with the energy ordering of states shown in Fig. 3.

IV. CORE POLARIZATION MODEL

To describe our observations we use a model based on the addition of two valence electrons to a spherically symmetric Ba^{2+} ion. Adding the first electron produces Ba^+ , which is isoelectronic with Cs, so the radial matrix elements for Ba^+ can be calculated using the Coulomb approximation, as is done for Cs. To Ba^+ we add the second electron, in a Rydberg state, to produce a Rydberg state of Ba. We assume that the second electron is in a high enough ℓ state that it does not penetrate the orbit of the first electron. We can then assume the two electrons to be distinguishable and ignore exchange.



FIG. 5. Geometry of the Ba atom having two electrons outside the closed shell Ba^{2+} core.

The geometry of the atom is shown in Fig. 5, where \bar{r}_1 and \bar{r}_2 are the locations of the two electrons relative to the Ba²⁺ core, θ_{12} is the angle between these vectors, and r_{12} is the separation between the electrons. The Hamiltonian for this atom is given by

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2f(r_1)}{r_1} - \frac{2f(r_2)}{r_2} + \sum_{k=0} \frac{r_1^k}{r_2^{k+1}} P_k(\cos \theta_{12}).$$
(3)

Here f(r)=1 for $r > r_c$, where r_c is the radius of the Ba²⁺ core and P_k is a Legendre polynomial. Consistent with our earlier assumption that $r_2 > r_1$ we take $f(r_2)=1$ and we relabel r_1 as r_i and r_2 as r_o in order to clearly distinguish the inner and outer electrons. In this case we can rewrite Eq. (3) as

$$H = H_0 + H_1, \tag{4}$$

where

$$H_0 = -\frac{\nabla_1^2}{2} - \frac{2f(r_i)}{r_i} - \frac{\nabla_2^2}{2} - \frac{1}{r_o}$$
(5)

and

$$H_1 = \frac{r_i}{r_o^2} P_1(\cos \theta_{12}) + \frac{r_i^2}{r_o^3} P_2(\cos \theta_{12}) + \dots$$
(6)

At this level of approximation H_1 consists of dipole and quadrupole terms. Ignoring for the moment H_1 we can see that the solutions to H_0 are products of Ba⁺ and hydrogen wave functions, i.e.,

$$|\Psi\rangle = |\Psi_{Ba}n\ell_{j}\rangle|\Psi_{H}n\ell\rangle. \tag{7}$$

The corresponding energies are

$$W_{n'\ell'_{j'}n\ell_K} = W_{n'\ell'_{j'}} - \frac{1}{2n^2},$$
(8)

i.e., the sum of the energies of the Ba⁺ core and the Rydberg electron.

Now we add H_1 as a perturbation. It introduces a first order quadrupole energy shift, W_{Q1} , and second order dipole and quadrupole energy shifts, W_{D2} and W_{Q2} , with the result that the energy is

TABLE II. Contributions to the quantum defects.

	$5d_{3/2}ngK = 5/2$		$5d_{3/2}nhK=7/2$	
	Adiabatic	Nonadia- batic	Adiabatic	Nonadia- batic
$W_{O1}n^3$	+0.0277	+0.0277	+0.0140	+0.0140
$\tilde{W_{D2}n^3}$	-0.0389	-0.0556	-0.0137	-0.0160
$W_{O2}n^3$	+0.0061	+0.0050	+0.0004	+0.00097
δ calculated	+0.0051	+0.0229	-0.0007	+0.0011
δ measured	+0.0187	+0.0187	+0.0027	+0.0027

$$W_{n'\ell'_{j'}n\ell_K} = W_{n'\ell'_{j'}} - \frac{1}{2n^2} + W_{Q1} + W_{D2} + W_{Q2}.$$
 (9)

We consider first the quadrupole term, W_{Q1} , which introduces a first order energy splitting of Rydberg levels with ionic cores. We assume that the Rydberg electron spin has no observable effect, and we ignore it. The resulting first order quadrupole energy shift of the Ba $5d_{3/2}n\ell$ states is given by

$$W_{Q1} = \left\langle 5d_{3/2}n\ell_K \left| \frac{r_i^2 \overline{C_1^{(2)}} \cdot \overline{C_2^{(2)}}}{r_o^3} \right| 5d_{3/2}n\ell_K \right\rangle.$$
(10)

Here $C_i^{(2)}$ are the spherical harmonic operators used by Edmonds [14] for the quadrupole interaction, and r_i and r_o are the radial positions of the inner and outer electrons. The matrix element of Eq. (10) consists of three factors, $\langle r_{5d}^2 \rangle = \langle 5d | r^2 | 5d \rangle$, $\langle n \ell | 1/r_o^3 | n \ell \rangle$ and an angular factor. For the permanent quadrupole moment of the Ba⁺ $5d_{3/2}$ ion we use the value of $\langle r_{5d}^2 \rangle = \langle 5d | r^2 | 5d \rangle = 17.44a_0^2$, obtained using a Coulomb wave function and a Numerov integration technique [15]. The hydrogenic values for $\langle n \ell | 1/r_o^3 | n \ell \rangle$ are $1/90n^3$ and $1/165n^3$ for $\ell = 4$ and 5 (see Ref. [16]). It is straightforward to evaluate the angular factor following Edmonds. The calculated values of $W_{Q1}n^3$ are given in Table II for the $5d_{3/2}ng K = 5/2$ and $5d_{3/2}nh K = 7/2$ states. We multiply W_{Q1} , W_{D2} , and W_{Q2} by n^3 to allow direct comparison to the observed quantum defects.

Both dipole and quadrupole terms of H_1 lead to second order energy shifts, W_{D2} and W_{Q2} , which can in many cases be expressed in terms of the dipole and quadrupole polarizabilities of the ionic core [17]. The second order dipole shift, W_{D2} , of the $5d_{3/2}n\ell_K$ state is given by [17]

$$W_{D2} = \sum_{n'',\ell'',j'',n',\ell'} \frac{\left| \left\langle n''\ell_{j''}'n'\ell_K' \right| \frac{r_i \overline{C_1^{(1)}} \cdot \overline{C_2^{(1)}}}{r_o^2} \right| 5d_{3/2}n\ell_K} \right\rangle \right|^2}{W_{5d_{3/2}n\ell_K} - W_{n''\ell_{j''}'n'\ell_K'}}.$$
(11)

The sums are understood to extend over the continua as well as over n' and n''. Allowed values of ℓ' are $\ell \pm 1$ and allowed values of ℓ'' are 1 and 3. The sum is over all Ba states to which the Ba $5d_{3/2}n\ell$ state is coupled by the dipole interaction. Since the allowed Ba⁺ states are the $np_{j''}$ and $nf_{j''}$ states, we can write Eq. (11) as MICROWAVE SPECTROSCOPY OF AUTOIONIZING...

$$W_{D2} = \sum_{n''} |\langle n''p|r_i|5d\rangle|^2 \sum_{j''n'\ell'=\ell\pm 1} \frac{|\langle n'\ell'_K|1/r_o^2|n\ell_K\rangle|^2}{W_{5d_{3/2}n\ell_K} - W_{n''p_{j''}n'\ell'_K}} |\langle p_{j''}\ell'_K|\overline{C_1^{(1)}} \cdot \overline{C_2^{(1)}}|d_{3/2}\ell_K\rangle|^2 + \sum_{n''} |\langle n''f|r_i|5d\rangle|^2 \\ \times \sum_{j''n'\ell'=\ell\pm 1} \frac{|\langle n'\ell'_K|1/r_o^2|n\ell_K\rangle|^2}{W_{5d_{3/2}n\ell_K} - W_{n''f_{j''}n'\ell'_K}} |\langle f_{j''}\ell'_K|\overline{C_1^{(1)}} \cdot \overline{C_2^{(1)}}|d_{3/2}\ell_K\rangle|^2.$$
(12)

We assume that the radial matrix elements are independent of spin for both electrons. To see how the sum of Eq. (12) can be reduced to the Ba⁺ dipole polarizability of Eq. (1) we consider W_{D2} for the $5d_{3/2}ng_K$ state as an example. In particular, let us consider only the term arising from the Ba⁺ $6p_{1/2}$ state. The allowed dipole couplings are to the $6p_{1/2}nf_K$ and $6p_{1/2}nh_K$ states which span an energy range W_o as shown in Fig. 6. It is important to keep in mind that $6p_{1/2}\epsilon h$ and $6p_{1/2}\epsilon f$ continua are included in the sums as well. If the energy range W_o spanned by the $n'\ell'$ states is small compared to the Ba⁺ $5d_{3/2}-6p_{1/2}$ interval W_i we can replace the denominator of Eq. (12) by $W_{5d_{3/2}} - W_{6p_{1/2}}$. We can then perform the sum over all the outer electron states using the formula of Van Vleck [17]

$$\langle n \ell | r^{2s} | n \ell \rangle = \sum_{n'} |\langle n' \ell' | r^s | n \ell \rangle|^2, \tag{13}$$

for any ℓ . The same procedure can be followed for all ion states, with the result that there is a common factor of $\langle n\ell | 1/r_o^4 | n\ell \rangle$ which can be removed from the sum over the Ba⁺ states. Equation (12) can then be written as

$$W_{D2_{ad}} = \left\langle n \, \ell \, \left| \frac{1}{r_o^4} \right| n \, \ell \right\rangle \left[\sum_{n''j''} \frac{|\langle n''p|r_i|5d\rangle|^2}{W_{5d_{3/2}} - W_{n''p_{j''}}} \sum_{\ell'=\ell\pm 1} |\langle n''p_{j''}\ell'_K|\overline{C_1^{(1)}} \cdot \overline{C_2^{(1)}}|5d_{3/2}\ell_K\rangle|^2 \right. \\ \left. + \sum_{n''j''} \frac{|\langle n''f|r_i|5d\rangle|^2}{W_{5d_{3/2}} - W_{n''f_{j''}}} \sum_{\ell'=\ell\pm 1} |\langle n''f_{j''}\ell'_K|\overline{C_1^{(1)}} \cdot \overline{C_2^{(1)}}|5d_{3/2}\ell_K\rangle|^2 \right].$$
(14)

The remaining sums over Ba⁺ states are recognized as twice the dipole polarizability. The Ba⁺ $5d_{3/2}$ state is not isotropic, so there is both a scalar and a tensor polarizability, not only a scalar polarizability as implied by Eq. (1).

As pointed out by Van Vleck and Whitelaw, a crucial approximation is that the range of energy spanned by the outer electron states is small compared to the energy spacing of the ionic states, i.e., $W_o \ll W_i$ (see Ref. [17]). This approximation is usually termed the adiabatic approximation since it corresponds to the outer electron's moving slowly in comparison to the inner electron. Representing W_{D2} by the scalar and tensor dipole polarizability of the ion is generally a reasonably good approximation since the dipole coupling couples $5d_{3/2}n\ell$ states to Rydberg states converging to ionic core states with opposite, odd, parity. Measurements of the $\Delta \ell$ intervals of Ba $6sn\ell$ states of $4 \le \ell \le 7$ can be represented by the adiabatic dipole polarizability to within 6%, 5%, 4%, and 3% for $\ell = 4, 5, 6, \text{ and } 7$ (see Ref. [19]). The nonadiabatic correction may be calculated by explicit calculation of W_{D2} and comparing it to the adiabatic model or, more elegantly, expressing the nonadiabatic correction in a form which has the same ℓ dependence as the ionic quadrupole polarizability of Eq. (1) (see Refs. [21,22]). For W_{D2} , the dipole case, the use of $\langle 1/r_o^4 \rangle$ in Eq. (14) should be a reasonable approximation since most the $Ba^+ n''p$ and n''f states are removed by more than 1 eV from the $5d_{3/2}$ state.

Inspection of the Ba⁺ oscillator strengths reveals that the dipole polarizability of the Ba⁺ $5d_j$ states can be calculated to within 2% if we only include the Ba⁺ $6p_j$ and $4f_j$ states [18]. Accordingly we have calculated both Eqs. (12) and (14) in

this approximation to determine W_{D2} and $W_{D2_{ad}}$. The $\langle n'\ell' | 1/r_o^2 | n\ell \rangle$ matrix elements were calculated numerically by Mathematica using hydrogenic wave functions [16]. We use hydrogenic energies in Eq. (12) except for the low lying nf states. For these states we have used the quantum defects $\delta_{6pnf}=0.2$ (see Ref. [23]) and $\delta_{4fnf}=0.6$ (see Ref. [24]) to represent their energies more accurately. Using this technique, we find the values of $W_{D2}n^3$ given in Table II. It is evident that even in the dipole case, a 25% correction to the adiabatic model is needed. The problem is that the largest contributions to the dipole polarizabilities for the $5d_{3/2}ng(h)$ states are from the lowest lying $6p_{1/2}nf(g)$ and $6p_{3/2}nf(g)$ states. These $6p_i n\ell$ states are roughly halfway between the Ba⁺ $6p_i$ limits and the $5d_{3/2}$ limit, with the result that the dipole polarizability is underestimated significantly in the adiabatic approximation.

The second order quadrupole shift W_{Q2} is given by

$$W_{Q2} = \sum_{n'',\ell'',j'',n',\ell'} \frac{\left| \left\langle n''\ell''_{j''}n'\ell'_{K} \middle| \frac{r_{i}^{2}\overline{C_{1}^{(2)}} \cdot \overline{C_{2}^{(2)}}}{r_{o}^{3}} \middle| 5d_{3/2}n\ell_{K} \right\rangle \right|^{2}}{W_{5d_{3/2}n\ell_{K}} - W_{n''\ell''_{j''}n'\ell'_{K}}}.$$
(15)

The sum is over all Ba states to which the Ba $5d_{3/2}n\ell$ state is coupled by the quadrupole interaction. Allowed values of ℓ' are ℓ , $\ell \pm 2$, and allowed values of ℓ'' are 0, 2, and 4. Equation (15) can be reexpressed in a form analogous to Eq. (12),

$$W_{Q2} = \sum_{n''} |\langle n''d|r_i^2|5d\rangle|^2 \sum_{j''n'\ell'=\ell,\ell\pm 2} \frac{|\langle n'\ell'_K|1/r_o^3|n\ell_K\rangle|^2}{W_{5d_{3/2}n\ell_K} - W_{n''d_{j''}n'\ell'_K}} |\langle d_{j''}\ell'_K|\overline{C_1^{(2)}} \cdot \overline{C_2^{(2)}}|d_{3/2}\ell_K\rangle|^2 + \sum_{n''} |\langle n''g|r_i^2|5d\rangle|^2 \sum_{j''n'\ell'=\ell,\ell\pm 2} \frac{|\langle n'\ell'_K|1/r_o^3|n\ell_K\rangle|^2}{W_{5d_{3/2}n\ell_K} - W_{n''g_{j''}n'\ell'_K}} |\langle g_{j''}\ell'_K|\overline{C_1^{(2)}} \cdot \overline{C_2^{(2)}}|d_{3/2}\ell_K\rangle|^2 + \sum_{n''} |\langle n''s|r_i^2|5d\rangle|^2 \sum_{j''n'\ell'=\ell,\ell\pm 2} \frac{|\langle n'\ell'_K|1/r_o^3|n\ell_K\rangle|^2}{W_{5d_{3/2}n\ell_K} - W_{n''g_{1/2}n'\ell'_K}} |\langle s_{1/2}\ell'_K|\overline{C_1^{(2)}} \cdot \overline{C_2^{(2)}}|d_{3/2}\ell_K\rangle|^2.$$
(16)

It is useful to write down the adiabatic approximation for W_{Q2} . We assume the energy denominators of Eq. (16) are given by the ionic energy spacings, and we omit the $5d_{3/2}n\ell$ states because they would yield infinity in the adiabatic approximation. The result is

$$W_{Q2_{ad}} = \left\langle n \, \ell \, \left| \frac{1}{r^{6}} \right| n \, \ell \right\rangle_{n''j''} \left[\frac{|\langle n''d|r_{i}^{2}|5d\rangle|^{2}}{W_{5d_{3/2}} - W_{n''d_{j''}}} \sum_{\ell'=\ell,\ell\pm 2} |\langle n''d_{j''}\ell'_{K}|\overline{C_{1}^{(2)}} \cdot \overline{C_{2}^{(2)}}|5d_{3/2}\ell_{K}\rangle|^{2} + \frac{|\langle n''g|r_{i}^{2}|5d\rangle|^{2}}{W_{5d_{3/2}} - W_{n''g_{j''}}} \sum_{\ell'=\ell,\ell\pm 2} |\langle n''g_{j''}\ell'_{K}|\overline{C_{1}^{(2)}} \cdot \overline{C_{2}^{(2)}}|5d_{3/2}\ell_{K}\rangle|^{2} + \frac{|\langle n''g|r_{i}^{2}|5d\rangle|^{2}}{W_{5d_{3/2}} - W_{n''g_{j''}}} \sum_{\ell'=\ell,\ell\pm 2} |\langle n''g_{j''}\ell'_{K}|\overline{C_{1}^{(2)}} \cdot \overline{C_{2}^{(2)}}|5d_{3/2}\ell_{K}\rangle|^{2} + \frac{|\langle n''g|r_{i}^{2}|5d\rangle|^{2}}{W_{5d_{3/2}} - W_{n''g_{1/2}}} \sum_{\ell'=\ell,\ell\pm 2} |\langle n''g_{1/2}\ell'_{K}|\overline{C_{1}^{(2)}} \cdot \overline{C_{2}^{(2)}}|5d_{3/2}\ell_{K}\rangle|^{2} \right|.$$

$$(17)$$

The remaining sums over Ba^+ are recognized as twice the quadrupole polarizability. Together these two factors comprise the quadrupole polarizability term of Eq. (1).

While using the dipole polarizability is often a good approximation, using the adiabatic quadrupole polarizability is often not, especially for Rydberg states converging to an isotropic or $\ell \neq 0$ ionic core. If the ion core does not have $\ell = 0$ it is quite likely that there is a fine structure splitting such as the Ba⁺ $5d_{3/2}$ - $5d_{5/2}$ splitting of 800 cm⁻¹. The Rydberg states converging to these two cores are coupled by W_{O2} , and the energy range spanned by the outer electron states in the sum of Eq. (16) can easily exceed the ionic splitting, with the result that the quadrupole polarizability model breaks down. To illustrate this point we show in Figs. 7 and 8 the values of $|\langle n'\ell' | 1/r_o^3 | n\ell \rangle|^2$ for n=45, ℓ =4 that contribute to W_{O2} in Eq. (16). In Fig. 7 we show the calculated matrix elements connecting the $5d_{3/2}ng$ to the $6s_{1/2}ng$ states, while in Fig. 8 we show the matrix elements connecting the $5d_{3/2}ng$ states to the $5d_{5/2}ng$ and *nd* states. Note that the Rydberg electron matrix elements connecting the $5d_{3/2}ng$ states to other $5d_{3/2}n\ell$ states are identical to the ones connecting the $5d_{3/2}ng$ state to the $5d_{5/2}n\ell$ states, only they are shifted in energy by the ionic splitting. The $\langle n'\ell' | 1/r_o^3 | n\ell \rangle$ matrix elements were calculated numerically by Mathematica using hydrogenic wave functions [16]. The values in Figs. 7 and 8 are normalized per unit energy (each boundstate value is multiplied by n'3 and given an energy width of n'^{-3} as is done by Gallagher *et al.* [19] and Fano and Cooper [20]).

Figure 7 clearly shows that in the quadrupole coupling to the Ba⁺ 6s core, the energy spread between the ion cores is comparable to the energy spread of the Rydberg electron matrix elements, in terms of Fig. 6 $W_o \approx W_i$. Here the use of the adiabatic model overestimates the influence of the 6snd states on the quadrupole polarizability since the major contribution to these matrix elements comes from the lowest lying 6*snd* states. This renders the use of the adiabatic approximation questionable at best.



FIG. 6. Energy level diagram showing the energy range W_o of the $6p_{1/2}nf$ and $6p_{nh}$ states to which the $5d_{3/2}ng$ states are coupled by the dipole interaction. Assuming the energy range W_o to be small compared to the ionic separation W_i is the basis of the adiabatic approximation.





FIG. 7. Energy distribution of the squared matrix element per unit energy $|\langle 45g | 1/r_o^3 | nd \rangle|^2$ which enters into the quadrupole interaction between the $5d_{3/2}ng K=5/2$ states and the 6snd K=5/2states. The Ba⁺ $5d_{3/2}$ energy is taken to be zero. Since the matrix elements are plotted per unit energy, the area of the curve is the squared matrix element. In this case the width of the distribution exceeds the ionic $6s_{1/2}$ - $5d_{3/2}$ splitting and the adiabatic approximation should not work. The matrix elements $|\langle 45g | 1/r_o^3 | ng \rangle|^2$ and $|\langle 45g | 1/r_o^3 | ni \rangle|^2$ are not plotted because the terms $|\langle s_{1/2}g(i)_K | C_1^{(2)} \cdot \overline{C_2^{(2)}} | d_{3/2}g_K \rangle|^2$ in Eq. (16) are zero and so these matrix elements do not contribute to the second order quadrupole energy shift.

Figure 8 removes any doubt as to the applicability of the adiabatic approximation. On the scale of the spread of the Rydberg electron matrix elements, the Ba⁺ $5d_{3/2}$ and Ba⁺ $5d_{3/2}$ cores are nearly degenerate. In fact, the separation between the ionic states is two orders of magnitude smaller than the energy spread of the Rydberg electron matrix elements. $W_o \ge W_i$, and the adiabatic approximation is clearly invalid. Stated another way, any nonadiabatic corrections will be as large as the adiabatic term itself. It is also evident that the nonadiabatic terms will be heavily dependent on *n*. As *n* decreases, there will be more states pushing the energy down and fewer pushing it up. Since properties of ions necessarily cannot depend on the *n* of the outer electron, any so called quadrupole polarizabilities extracted in this way cannot be actual properties of the ion core.

We have calculated both W_{Q2} and $W_{Q2_{ad}}$ by considering only Ba states with Ba⁺ ion core states of $\delta s_{1/2}$ and $5d_j$ since those terms have the largest quadrupole matrix elements and smallest energy denominators. We have again used hydrogenic wave functions and energies except for the low lying *nd* and *nf* states. For these states we have used the quantum defects $\delta_{6snd}=2.7$ (see Ref. [25]), $\delta_{5dnd}=2.65$ (see Ref. [11]), $\delta_{6snf}=0.2$ (see Ref. [26]), and $\delta_{5dnf}=0.1$ to represent their energies more accurately. The resulting values are given in Table II. Adding $W_{Q1}n^3$, $W_{D2}n^3$, and $W_{Q2}n^3$, gives the total calculated quantum defects for the $5d_{3/2}ng$ K=5/2 and $5d_{3/2}nh$ K=7/2 states, and they are in reasonable agreement with the observed ones as shown by Table II.

FIG. 8. Energy distribution of the squared matrix element per unit energy $|\langle 45g | 1/r_o^3 | n\ell \rangle|^2$ which enters into the quadrupole interaction between the $5d_{3/2}45g K=5/2$ states and the $5d_{5/2}n\ell K$ =5/2 states. The Ba⁺ $5d_{3/2}$ energy is taken to be zero, and the Ba⁺ $5d_{5/2}$ energy, 0.0036, is not visibly different on the scale of this figure. Since the matrix elements are plotted per unit energy, the area of the curve is the squared matrix element. In this case the width of the distribution exceeds the ionic $5d_{5/2}$ - $5d_{3/2}$ splitting by two orders of magnitude and the adiabatic approximation is completely invalid. The matrix elements plotted here are $|\langle 45g | 1/r_o^3 | nd \rangle|^2$ (dashline) and $|\langle 45g | 1/r_o^3 | ng \rangle|^2$ (solid line). The matrix element $|\langle 45g | 1/r_o^3 | ni \rangle|^2$ is not plotted because the term $|\langle d_{5/2}i_K | \overline{C_1^{(2)}} \cdot \overline{C_2^{(2)}} | d_{3/2}g_K \rangle|^2$ in Eq. (16) is zero and so this matrix element does not contribute to the second order quadrupole energy shift.

In contrast, the adiabatic approximation leads to poor agreement.

The breakdown of the adiabatic model in the quadrupole case is clearly more severe than in the dipole case. The corrections to the adiabatic quadrupole term are as large as the quadrupole term itself, so large as to render the adiabatic quadrupole polarizability meaningless.

The fact that the adiabatic quadrupole polarizability is almost meaningless for the Ba $5d_{3/2}$ states is not really a surprise. In the recent analysis of Ba $6sn\ell$ states of $\ell=6$ it was noted that the quadrupole polarization energy was "quite problematic," largely because of the proximity of the Ba⁺ $5d_j$ states to the Ba⁺ $6s_{1/2}$ state [27]. In that case the separation of the ionic states is 5000 cm⁻¹, while in our $5d_j$ case it is 800 cm⁻¹.

A potential problem with the polarization model, especially for the quadrupole interaction is the interaction between overlapping series. For example, series converging to the $5d_{3/2}$ and $5d_{5/2}$ limits interact, and in the energy range below both limits there are local perturbations to the energy levels that are often displayed graphically as Lu-Fano plots. These local perturbations can be removed by "deperturbing" the series, as is done in molecular spectroscopy [28], but a better approach is a coupled channel scattering approach, i.e., quantum defect theory [29–31]. Furthermore, if the ion is anisotropic, i.e., has $j \ge 1$, as does the Ba⁺ $5d_{3/2}$ state, the sum for W_{Q2} includes states converging to the same ionic core. These states contribute substantially to the sums of Eq. (16), but the ion core state cannot contribute to its own quadrupole polarizability.

The only other spectroscopy of levels converging to an anisotropic core is the study of the Ne n=10 levels converging to the ${}^{2}P_{3/2}$ ion core. In fitting the data the $\langle 1/r^{6} \rangle$ contribution was attributed to the combination of the quadrupole polarizability and the nonadiabatic correction to the dipole polarizability. The uncertainty was ~10%, and no attempt was made to separate the two contributions. In the case of Ne, it is interesting to consider the effect of the nearby ${}^{2}P_{1/2}$ ion state, which is 782 cm⁻¹ above the ground state. The nearest ${}^{2}P_{1/2}n\ell$ states to the ${}^{2}P_{3/2}$ 10 ℓ states are the ${}^{2}P_{3/2}11\ell$ states, however, lie only 26 cm⁻¹ below the ${}^{2}P_{1/2}8\ell$ states, and might exhibit quite different shifts due to the near resonant quadrupole couplings. That is, they might be a clear demonstration of the local perturbations described in the previous paragraph.

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V. CONCLUSION

autoionizing Rydberg states. While these measurements

alone do not allow us to extract definitively the properties of

the Ba⁺ $5d_{3/2}$ core, they are a step toward a systematic study

of such states. Furthermore, they highlight the fact that the

adiabatic core polarizability approach, widely used to inter-

pret microwave resonance data from Rydberg states with iso-

topic cores, is of questionable value for extracting the quad-

rupole polarizability from Rydberg states with anisotropic

cores.

We report the microwave resonance spectroscopy of