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Optical isotope shifts and hyperfine structure in $\lambda 553.5$ nm of barium

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The structure of the resonance line $\lambda 553.5$ nm of Ba I has been studied by means of Doppler-free spectroscopy. Dye laser light was scattered resonantly from an atomic beam containing the natural mixture of isotopes; the spectra were recorded digitally and analysed by computer. The main object was to provide data to reduce uncertainties due to electronic calculations in the extraction of nuclear data from optical measurements. The isotope shifts (MHz), relative to ^{138}Ba , are ^{137}Ba , -214.7 (5); ^{136}Ba , -127.5 (13); ^{135}Ba , -258.7 (7); ^{134}Ba , -142.8 (12). The minus signs indicate that ^{138}Ba has the lower frequency in each case. These results are combined with muonic X-ray, electronic X-ray and other optical data to extract changes in mean square radius of the nuclear charge distribution.

The hyperfine splitting factors ^{135}A and ^{135}B were found to be -97.76 (14) MHz and 32.29 (47) MHz respectively. From an analysis of these and other results for the $6s6p$ configuration we obtain the quadrupole moment of ^{135}Ba (uncorrected for quadrupole shielding) to be 0.195 (40) barn ($1 \text{ barn} = 10^{-28} \text{ m}^2$).

1. INTRODUCTION

We have studied the resonance line $\lambda 553.5$ nm of Ba I ($6s^2 1S_0 - 6s 6p 1P_1$) by crossing a tunable dye laser with an atomic beam and observing the fluorescence from the upper level (see, for example, Broadhurst *et al.* 1974). The purpose of the experiment is to measure the isotope shift and hyperfine structure in this line to high precision.

The use of an atomic beam to reduce the Doppler broadening of an optical line to a very low value is, of course, well known (see, for example, Jackson & Kuhn 1935), and indeed Jackson & Duong Tuan (1964, 1966) have used an atomic beam in absorption with a conventional light source to investigate the structure of the resonance line of Ba I. However, the method which we have applied, that of scanning the structure with a dye laser and analysing the entire spectral profile of the fluorescent light, gives an order of magnitude improvement in accuracy. Previous work on the structure of the $6s 6p 1P_1$ level also includes that of Swagel & Lurio (1968) by double resonance and that of Kluge & Sauter (1974) by level crossing. Nowicki *et al.* (1977) have measured isotope shifts of radioactive isotopes of Ba by laser spectroscopy.

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Measurements of optical isotope shifts have contributed to our understanding of nuclear charge distributions (see, for example, Barrett & Jackson 1977, Heilig & Steudel 1974) and of atomic structure (Bauche & Champeau 1976). The main reason for interest in barium ($Z = 56$) is that changes in the nuclear charge distribution with neutron number can be studied over a large range of isotopes which spans a shell closure. The calculation of electronic factors associated with the optical transitions is a major source of uncertainty in the interpretation of isotope shifts; in order to reduce this uncertainty as far as possible it is desirable to find empirically the relations between the factors for different spectral lines. For this purpose one needs the highest possible precision of measurement, but the range of nuclei studied need not be large. Our own work has been concerned only with the more abundant stable isotopes in their natural isotopic mixture.

Our experimental method differs from that of previously published work on laser spectroscopy mainly in the data analysis. The spectral components are only partially resolved in $\lambda 553.5$ nm, even with a line width close to the limit imposed by natural broadening; so to achieve high precision we had to allow for several small effects which influence the profile, particularly those which depend on laser power. Concurrently with our work a similar but independent experiment on $\lambda 553.5$ nm has been carried out in Karlsruhe (Nowicki *et al.* 1978). The latter work is primarily to give results for rare and radioactive isotopes, but recently data for the nuclei studied here have also been obtained. Their results show a large measure of agreement with our own, and this is particularly gratifying in view of the relative novelty of dye laser experiments and the consequent lack of experience in dealing with the problems they raise.

We have measured the positions relative to ^{138}Ba (71.66 % abundant in the natural mixture) of ^{137}Ba (11.32 %), ^{136}Ba (7.81 %), ^{135}Ba (6.59 %) and ^{134}Ba (2.4 %). Both odd isotopes have nuclear spin $I = \frac{3}{2}$, giving each a three-component hyperfine structure in $\lambda 553.5$ nm; we have also made measurements of these structures. That so much precise information can be acquired from the spectrum of the natural mixture of isotopes, in which the resolution is incomplete, is due to three main factors: the narrow line width of the dye laser excitation, the selective study of odd isotopes by an appropriate choice of polarization of the laser light (Rasmussen *et al.* 1974) and the detailed treatment of systematic effects.

In § 2 we describe the experiment, and in § 3 the data analysis. The results are given in § 4 and discussed in § 5.

2. EXPERIMENTAL METHOD

(a) Summary

The experimental arrangement is shown schematically in figure 1. The beam of light from a tunable dye laser travelled along Oy and intersected a beam of barium atoms directed along Ox ; a photomultiplier detected the fluorescent light emitted along Oz . In an experimental run, the frequency of the laser light was scanned at a

rate of about 2.5 MHz s^{-1} through the frequency range occupied by the spectral components in $\lambda 553.5 \text{ nm}$ (about 0.6 GHz). The signal was recorded in digital form. A frequency calibration signal, recorded simultaneously, consisted of the intensity of the laser light transmitted through a reference etalon, i.e. a stabilized confocal cavity with mirrors separated by $1.9343(5) \text{ m}$. This gave frequency markers $38.748(10) \text{ MHz}$ apart. The data were analysed by computer fitting.

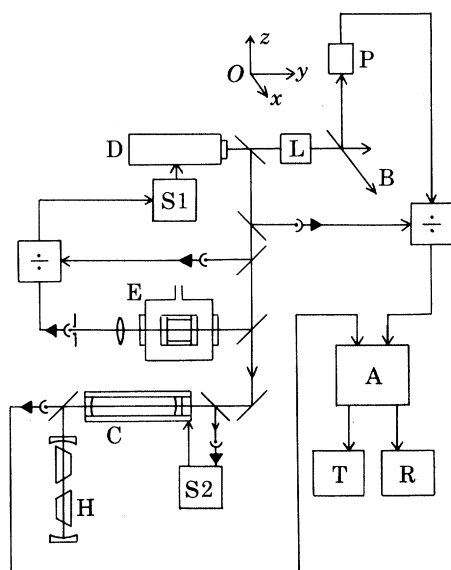


FIGURE 1. Schematic diagram of apparatus. Excitation and detection: D, dye laser. B, barium beam. P, photomultiplier. L, beam expander and polarizing components. Calibration and control: E, pressure-scanned etalon. S1, laser frequency servo-control. C, 2 m confocal cavity. S2, cavity length servo-control. H, stabilized helium-neon laser. Signal processing and recording: A, analogue to digital converter with analogue output to R, chart recorder, and digital output to T, tape punch.

(b) *The light source and calibration system*

These components were mounted on a marble slab supported by air bearings. The Spectra-Physics 580A jet-stream dye laser was pumped by an argon ion laser. Scanning of the laser frequency was carried out by locking it to the side of the peak of an external plane Fabry-Perot etalon, which was then pressure-scanned. This etalon had a spacing of 12 cm and a finesse of 50 . The ratio of the transmitted to the incident intensity was kept constant by a servo-loop controlling the length of the laser cavity; the 'jitter' about this ratio showed that the effective width of the spectral distribution from the laser due to such excursions was about 3 MHz .

The fundamental reference frequency was provided by a helium-neon laser, stabilized by saturated absorption in iodine vapour contained in an intra-cavity cell (Rowley & Wallard 1973). The frequency modulation used to lock to the iodine feature was also employed to lock the length of the reference etalon so that one of

its transmission maxima coincided with the mean helium-neon laser frequency. The marker fringes formed by the dye laser light during a scan were recorded without normalization to allow the intensity variation with frequency to be monitored in each run; the intensity was found to remain constant to within about 5%. A typical set of marker fringes is shown in figure 2. The finesse of the reference etalon was measured to be 13 (2), so the 6 MHz width (f.w.h.m.) of the fringes includes a contribution of about 3 MHz from the cavity itself, the remainder being consistent with the spectral width attributed to laser jitter.

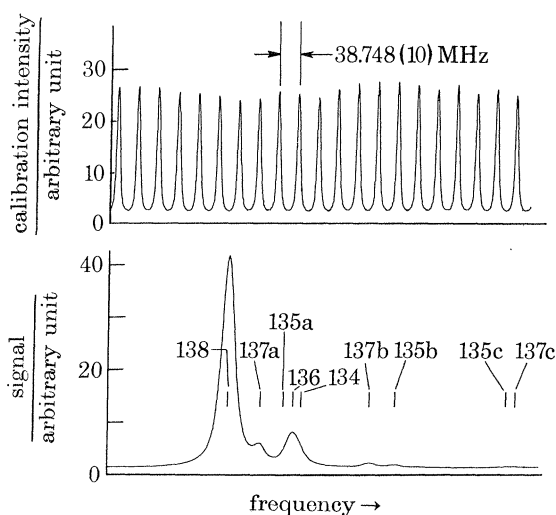


FIGURE 2. Computer plot of unprocessed data from a single scan with simultaneously recorded calibration fringes which are later used to linearize the frequency scale. The positions of the components are shown; the hyperfine structure of the odd isotopes is shown in the inset to figure 3. The recording is of the type used to measure the positions of the even isotopes (see § 4).

(c) *The interaction region and the recording of data*

The laser beam incident on the interaction region was plane polarized, and had a power of about 0.1 mW in a cross-sectional area of 1 cm². The collimation ratio of the barium beam was 68:1, and the density of barium atoms about 10⁹ atoms cm⁻³. The interaction region was imaged on the photocathode of an E.M.I. 9658R photomultiplier. The output was divided by the signal from a photodiode monitoring the intensity of the laser light; this normalized signal was then digitized and recorded on paper tape at intervals of 0.4 s, corresponding to about 1 MHz separation of data points (a typical scan is shown in figure 2). Every data point was recorded together with the digitized calibration from the marker fringes.

(d) Preliminary data processing

The data for each run were first reduced by computer to a form suitable for analysis, as follows. The marker fringes were processed to determine the frequency scale. The centre of gravity of the data points within each fringe was found, and a cubic calibration curve was then fitted to the positions of the fringes. The r.m.s. deviation from the cubic was typically 0.25 MHz.

After calibration, the data points representing the barium spectrum were condensed to give a smaller number of points just 5 MHz apart. Examples of spectrograms of this type are shown in figures 3 and 4. The analysis of the processed experimental data (which we denote by I_{exp}) was then carried out by matching the profile as closely as possible by a theoretical profile I_{th} , synthesized by computer. In the next section we discuss the construction of this theoretical profile.

3. THE FLUORESCENT INTENSITY DISTRIBUTION

The accuracy with which isotope shifts and hyperfine structure constants can be derived from an observed spectrum depends on how well the spectrum can be fitted with the synthesized distribution I_{th} . It is desirable to reduce the systematic errors introduced by misrepresentation of the experimental profile to the level of other sources of uncertainty in the experiment.

In many high resolution experiments, it is not necessary to consider the processes giving rise to the shapes of the individual components present in the spectrum at all; it is sufficient to represent them all by the same empirical function, provided that this gives a good fit (see, for example, Brimicombe *et al.* 1976). However, in the present work, the profile varies from one component to another, and to take this into account we need to understand the mechanisms which influence the line-shape. These are of two types.

(i) Those which produce effects common to all spectral components present, whether due to odd or even isotopes; they can be described in terms of three basic distributions, the natural line-shape of a stationary atom, the laser intensity distribution, and the distribution arising from the spread of atomic velocity components in the line of sight (Minkowski & Bruck 1935).

(ii) Those which affect different components in different ways. These involve polarization and optical pumping effects. We discuss these in turn.

The even isotopes can be described entirely in terms of mechanisms of type (i), apart from an overall intensity scaling factor due to polarization of the incident light. Spectra of the type shown in figure 2 permit a study of the even isotope profile, since they are dominated by the component due to ^{138}Ba , one wing of which is almost entirely free from perturbations by neighbouring components. With the low laser intensity used in our experiments, stimulated emission is quite negligible, and the width of the profile is mainly due to natural broadening (19 MHz out of 29 MHz), which gives a Lorentzian line-shape. We assume no knowledge of the

form of the other two distributions; however, the final profile was itself found to be quite close to Lorentzian. We therefore constructed a theoretical profile as follows: it was assumed that the laser intensity distribution could be represented by a Lorentzian of width 3 MHz, and this was convolved with a distribution over frequency (ν) having the form of a modified Lorentzian

$$f(\nu - \nu_0) \propto \{(|\nu - \nu_0|)^p + (\frac{1}{2}\Gamma)^p\}^{-1} \quad (1)$$

which is to represent empirically the effect of Doppler motion in a highly collimated atomic beam. The values of p and Γ were then chosen to give the best fit to the data; values of p between 2 and 3 were obtained in practice and Γ was about 6.8 MHz. Although the function (1) is primarily to take account of velocity spread in the direction Oy , it can also absorb small errors in our description of the profile, owing, for example, to misrepresentation of the laser distribution. The even isotopes in any given spectrogram were thus all assumed to have the same line-shape (apart from intensity scaling), formed by the convolution of a Lorentzian of width 22 MHz, representing the natural line-shape and laser distribution, with the function (1). This profile was therefore specified by the values of two parameters, p and Γ , which were allowed to 'float' in the computer fitting.

For the odd isotopes, the type (ii) mechanism of optical pumping introduces a third line-shape parameter. We describe here the effect in physical terms, since the formal analysis is rather specialized. Suppose the frequency of the incident plane-polarized light is close to that of a hyperfine component $F_i - F_f$, where F_i , F_f are the total angular momenta of the ground and excited hyperfine levels respectively. Then in crossing the interaction region, an atom may undergo several successive processes of absorption of plane-polarized light and subsequent spontaneous emission back to the ground level (we recall that stimulated emission is negligible). This causes a redistribution of the atoms among the degenerate ground level magnetic substates $|F_i M_i\rangle$, and in an atomic beam there is no relaxation mechanism to alter appreciably the resulting population distribution. Since the probability for excitation by plane-polarized light depends on M_i , the excitation rate for a given atom is a function of the length of time it has been in the interaction region (as well as of the laser intensity). The nett fluorescent intensity is thus modified by the pumping process. The effect distorts the line profile because the pumping efficiency varies with laser frequency; for example, if this is far enough away from line centre for atoms to undergo on average less than one excitation in crossing the interaction region, pumping has very little effect on the fluorescent intensity.

After applying the theory of optical pumping in detail and then averaging over the time-of-flight distribution in the atomic beam, we introduced a new parameter, μ , to take account of optical pumping in the description of the line profile; μ is the mean number of excitations undergone by an atom of an even isotope in crossing the interaction region when the laser frequency coincides with the natural frequency of the transition. The dependence of the profile on μ is different from one hyperfine

component to another; pumping effects are completely absent for the even isotopes because the ground level is then nondegenerate, while for the odd isotopes the transition to $F_1 = \frac{1}{2}$ shows the greatest distortion. In this case, excitation is possible from only two of the ground level substates, and once an atom has been pumped out of these states it ceases to contribute at all to the fluorescence. Figure 4 shows a trace obtained with $\mu = 60$; this differs considerably from the spectrogram shown in figure 3 ($\mu = 4$), the change in shape of the $F_1 = \frac{1}{2}$ transitions being especially marked. Our final data were taken with values of μ up to 10, but the accuracy with which the recording in figure 4 has been fitted gives confidence in the adequacy of our line-shape formulae to reproduce profiles with smaller distortion from pumping effects.

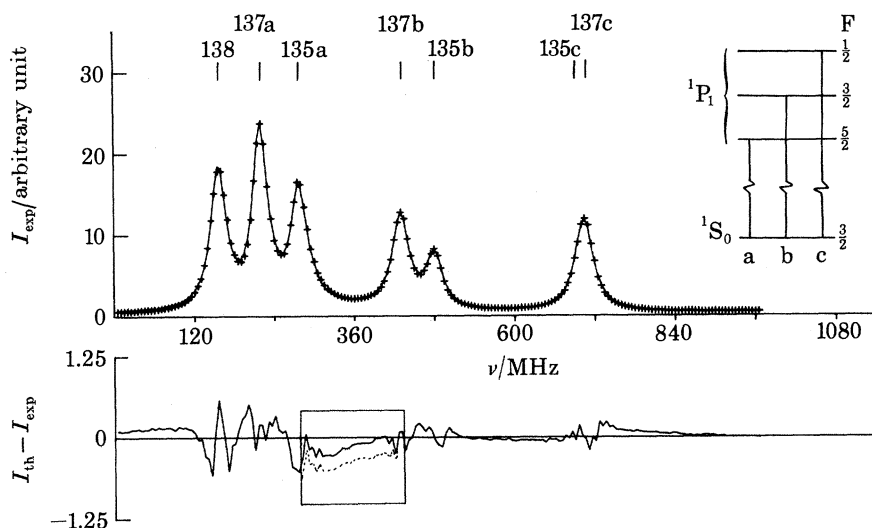


FIGURE 3. Example of data from a single run after processing. The experimental points I_{exp} (the crosses) are 5 MHz apart. The continuous curve gives I_{th} . The positions of the components are shown; in this case the polarization of the exciting light was chosen so as to reduce the relative intensities of the even isotopes (see § 4). The inset shows the hyperfine structure of the odd isotopes.

The residual curve of $I_{\text{th}} - I_{\text{exp}}$ against frequency (see text) is plotted below I_{exp} on a scale enlarged by a factor of 8. The dashed curve in the boxed section shows the poorer fit obtained between the stronger hyperfine components when interference between different routes for excitation and decay is ignored (see § 3).

We note that strictly there is an additional pumping process which occurs for all isotopes, due to the decay from $6s\ 6p\ ^1P_1$ to the metastable level $6s\ 5d\ ^1D_2$. Estimates of the branching ratio to the 1D_2 level vary considerably (Bernhardt 1976), but it is certainly low enough for the transitions to give rise to negligible changes in our observed profiles.

The other mechanism of type (ii) is the effect on the observed intensity of the direction of polarization of the laser light. This effect can be calculated exactly; for the even isotopes in $\lambda 553.5\ \text{nm}$, the result is very simple, giving a smooth variation

from a maximum to a minimum of intensity (zero but for the solid angle accepted by the detection system) as the electric vector is rotated from Ox to Oz in figure 1. For the odd isotopes, the expressions are complicated by the interrelation with the optical pumping described above.

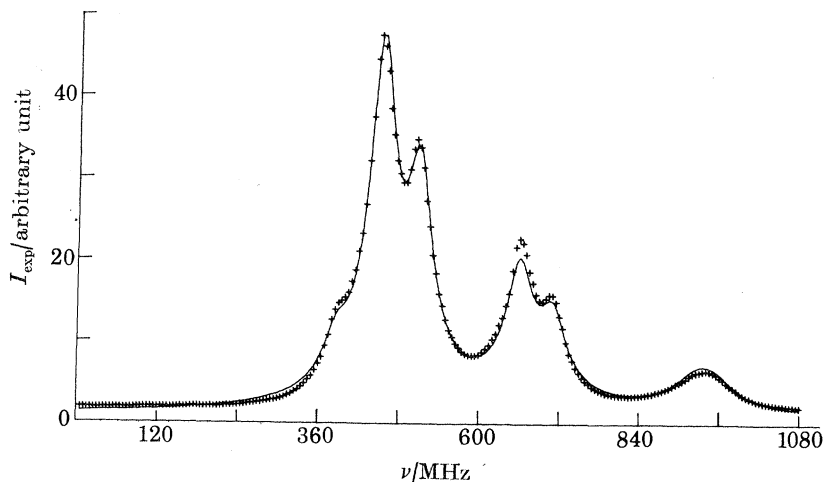


FIGURE 4. An example of a recording made with laser polarization similar to that in figure 3 but with high laser intensity. The crosses are the experimental points, separated by 5 MHz; the continuous curve is the theoretical profile. Recordings of this type were used only to check the theoretical description of the profile.

Finally, we found that it was not sufficient to represent the three hyperfine components of an odd isotope by three independent profiles, and the reason is this: it is well known from level-crossing experiments that observable interference effects arise from the overlap of atomic energy levels subject to homogeneous broadening. When the overlap is partial, as in the troughs between the peaks of a pattern of hyperfine components, the interference effects still give a contribution to the intensity. In our work a treatment of this effect was incorporated in the analysis; without it we obtained a poorer fit to the data, as illustrated in the boxed section of figure 3.

4. RESULTS

The results are given in table 1. They were derived from two types of spectrogram, differing in the direction of the plane of polarization of the exciting light. To study the hyperfine structures of the odd isotopes and measure odd-even shifts, we chose the polarization direction to lie close to, but not coincident with, Oz . The even isotopes were then greatly suppressed, but the component due to ^{138}Ba was still intense enough for the odd-even shifts to be measured accurately. We measured the even-even shifts with the exciting light polarized along Ox . We describe the analysis of each type of spectrogram separately.

(a) 'Odd' traces

The final data were derived from the analysis of 14 runs. The conditions of excitation (laser power and direction of the plane of polarization of the laser light) were varied to give a check of systematic error. A typical recording is shown in figure 3; apart from ^{138}Ba , the even isotopes are present in such small quantities that the analysis is insensitive to their positions. The separations of the main components present are thus determined by six quantities; the isotope shifts ^{138}Ba – ^{137}Ba and ^{138}Ba – ^{135}Ba , and the A and B hyperfine splitting factors of the odd isotopes. These cannot all be determined to high precision from the analysis because two of the seven principal components are completely unresolved; we can thus find the values of only five structure parameters without undue reliance on the assumed line-shape. Fortunately, it is only necessary to determine four, since the ratios $^{137}A/^{135}A$ and $^{137}B/^{135}B$ are precisely known from double resonance experiments in the $6s\ 6p\ ^3P_1$ level (zu Putnitz 1963; see also von Oppen 1968). We therefore fixed these ratios at their known values and found from our spectrograms values of the two odd-even shifts and of A and B for ^{135}Ba .

TABLE 1. ISOTOPE SHIFTS AND HYPERFINE STRUCTURE
IN $\lambda 553.5$ nm OF Ba I

Isotope shifts/MHz	
^{138}Ba – ^{135}Ba centre of gravity	– 258.7 (7)
^{138}Ba – ^{137}Ba centre of gravity	– 214.7 (5)
^{138}Ba – ^{134}Ba	– 142.8 (12)
^{138}Ba – ^{136}Ba	– 127.5 (13)

Hyperfine structure splitting factors/MHz

$$^{135}A (^1P_1) = -97.76 (14)$$

$$^{135}B (^1P_1) = 32.29 (47)$$

The values of the splitting factors for ^{137}Ba can be found by using the ratios

$$^{137}A/^{135}A = 1.11891 (3)$$

$$^{137}B/^{135}B = 1.537 (2)$$

measured for the 3P_1 level by zu Putnitz (1963).

The uncertainty in this experiment is partly statistical and partly due to the imperfect description of the line profile. In the case of the odd traces, there is evidence that the former dominates. In particular, when the ratios $^{137}A/^{135}A$ and $^{137}B/^{135}B$ were allowed to vary in the analysis so that their values could be determined, the results were in good agreement with the double resonance data despite their dependence on the positions of unresolved components.

The final results in table 1 are weighted means of the results from the different runs; the quoted errors are one standard deviation.

(b) 'Even' traces

The isotope shifts $^{138}\text{Ba}-^{136}\text{Ba}$ and $^{138}\text{Ba}-^{134}\text{Ba}$ were obtained from the analysis of four even traces, with the results obtained for the odd isotopes as fixed parameters in the least-square fits. The other stable isotopes are present in quantities too small for them to be located in the presence of the more abundant ones.

For these even traces there is a similarity between the curves of $I_{\text{th}}-I_{\text{exp}}$ against frequency, and this indicates the existence of small systematic errors in I_{th} . Since the pattern is dominated by the profile of the abundant isotope ^{138}Ba , even slight errors in the description of this profile may be compensated in the computer analysis by apparent shifts in the positions of the smaller components. From a study of the shape of the curve of $I_{\text{th}}-I_{\text{exp}}$ against frequency we have estimated the magnitude of such spurious displacements to be of the order of 0.7 MHz. We therefore make allowance for this effect by quoting the uncertainty as one standard deviation augmented by 0.7 MHz.

The even-even shifts are thus determined with rather poorer accuracy than the odd-even shifts for two reasons: (i) while the even isotopes can be almost completely suppressed with respect to the odd by choice of polarization, the converse is not true; (ii) the various even isotopes have very different natural abundances.

5. DISCUSSION

(a) *Hyperfine structure*

The results for ^{135}A and ^{135}B presented in this work are in agreement with those of previous experiments (Jackson & Duong Tuan 1964; Kluge & Sauter 1974) and they are much more precise. They also agree with those results obtained shortly after our experiment by Nowicki *et al.* (1978). Even with precise data, however, there is a difficulty in making an accurate determination of the nuclear quadrupole moment, a matter which has had a long history.

It is now well known that the 6s 6p configuration of barium is not well described by the original theory of Breit & Wills (1933) because the central-field approximation is not a good one in this case. Furthermore, there are not enough data for an application of the more general theory of Sandars & Beck (1965), though we note that it has been possible for Gustavsson *et al.* (to be published) to analyse the hyperfine structure of the 6s 5d configuration with an effective Hamiltonian. In the following, therefore, we apply the formalism and approach of Lurio (1966), who has set out an empirical modification to the Breit and Wills theory with different radial wave functions for the singlet and triplet states. These functions are assumed to be proportional to each other for small values of r with the consequence that for the p-electron a parameter λ_p is introduced:

$$\lambda_p = \langle r^{-3} \rangle_p^{\text{ST}} / \langle r^{-3} \rangle_p^{\text{TT}} = \langle r^{-3} \rangle_p^{\text{SS}} / \langle r^{-3} \rangle_p^{\text{ST}}, \quad (2)$$

where the superscripts S and T refer to the singlet and triplet wave functions

implicit in the averaging of r^{-3} . With the assumption that this single parameter is common to the magnetic dipole and electric quadrupole h.f.s. interactions, the single-electron h.f.s. constants for the p-electron are

$$a_j^{SS} = \lambda_p a_j^{ST} = \lambda_p^2 a_j^{TT} \quad (\text{magnetic dipole}), \quad (3)$$

$$b_j^{SS} = \lambda_p b_j^{ST} = \lambda_p^2 b_j^{TT} \quad (\text{electric quadrupole}). \quad (4)$$

Kluge & Sauter (1974) write, in addition, for the s-electron

$$a_s^{ST} = \lambda_s a_s^{TT}, \quad (5)$$

thereby introducing another parameter in the magnetic dipole h.f.s.

The parameter λ_p has been discussed in respect of fine structure, where a (possibly different) value of $\langle r^{-3} \rangle$ appears, by King & Van Vleck (1939) and by Vainshtein & Poluetkov (1962). From the fine structure one obtains λ_p (f.s.) = 0.84. For the hyperfine structure in intermediate coupling the equations relating $B(^1P_1)$ and $B(^3P_1)$ to $b_{\frac{3}{2}}^{TT}$ are sensitive to the value of λ_p and so they afford a good method for determining λ_p (h.f.s.). For the intermediate coupling coefficients α and β defined by

$$\begin{aligned} |^3P_1\rangle &= \alpha|^3P_1\rangle_{LS} + \beta|^1P_1\rangle_{LS} \\ |^1P_1\rangle &= -\beta|^3P_1\rangle_{LS} + \alpha|^1P_1\rangle_{LS} \end{aligned}$$

we follow Swagel & Lurio (1968) in using $\alpha = 0.9950$, $\beta = -0.0995$ derived from lifetime measurements. From our experimental value of +32.29 MHz for the quadrupole constant $^{135}B(^1P_1)$ and that of zu Putlitz (1963), -27.08 (2) MHz for $^{135}B(^3P_1)$ we obtain a value of λ_p (h.f.s.) = 0.796 (11). The limit of error corresponds to that for $B(^1P_1)$, the less accurate of the two experimental numbers, and does not depend at all strongly on the choice of α and β . It seems clear, therefore, that in the approach which has been adopted by Lurio, λ_p (h.f.s.) is not the same as λ_p (f.s.) but differs from it by about 5.5 %.

The introduction of λ_p allows the two experimental quantities $B(^3P_1)$ and $B(^1P_1)$ to be reconciled with a single value of $^{135}b_{\frac{3}{2}}^{TT}$ which we find to be 48.7 (1) MHz. To evaluate the quadrupole moment from $b_{\frac{3}{2}}^{TT}$ one needs a value for $\langle a_0^3 r^{-3} \rangle$, and it is usual to prefer a value from h.f.s. measurements. But in the absence of sufficient data on the magnetic dipole interaction (in particular, the h.f.s. of the 3P_2 level has not been measured) we take the value $\langle a_0^3 r^{-3} \rangle = 2.36$ from the fine structure. In deriving this value we took account of spin-other-orbit interaction, but not of spin-spin interaction, and put $Z_1 = 52$ with appropriate relativistic correction (Kopfermann 1958). Hence ^{135}Q (uncorrected) = 0.195 (40) barn, uncorrected for quadrupole shielding. The conservative limits of error are estimated to allow for the uncertainties in the method of evaluation of the quadrupole moment from the data. This result agrees with that calculated by Ma & zu Putlitz (1976).

An attempt to evaluate λ_s from the magnetic dipole h.f.s. is much less reliable since, in particular, λ_s depends strongly on the coefficient $2\alpha\beta$ in the cross-term in intermediate coupling. If we take, for ^{135}Ba , $a_{\frac{3}{2}}^{TT} = 70.6 \pm 5$ MHz as estimated from the value of $\langle a_0^3 r^{-3} \rangle = 2.36$ appropriate to the fine structure, and assume

further that $a_{\frac{3}{2}}^{\text{TT}} = 5a_{\frac{3}{2}}^{\text{TT}} \theta$ where the relativistic factor $\theta = 1.3$, then we find from the experimental values $^{135}\text{A } ({}^3\text{P}_1) = 1028.31 \text{ MHz}$ (zu Putlitz 1963) and $^{135}\text{A } ({}^1\text{P}_1) = -97.76 \text{ MHz}$ (this paper)

$$^{135}a_{\frac{3}{2}}^{\text{TT}} = 2672 (75) \text{ MHz}$$

and

$$\lambda_{\text{s}} \approx 1.01.$$

The uncertainties in $2\alpha\beta$ and in $a_{\frac{3}{2}}^{\text{TT}}$ are such that λ_{s} could be as high as 1.15. But there does not seem to be enough experimental evidence for any definite conclusion that λ_{s} differs markedly from unity (see, however, Kluge & Sauter 1974, who estimated $\lambda_{\text{s}} = 1.19$ from less recent data and Klapisch 1967, who gives $\lambda_{\text{s}} = 1.18$ as a theoretical value).

(b) Isotope shift

As with the results for the hyperfine structure, the isotope shift data are considerably more precise than any published measurements for barium (see, for example, Jackson & Duong Tuan 1966) and agree with those obtained subsequently by Nowicki *et al.* (1978).

The object of measuring isotope shifts is to derive information about the nuclear charge distribution. In order to do this one needs to know certain electronic factors (defined below) associated with the particular transition. For $\lambda 553.5 \text{ nm}$ these factors cannot be calculated reliably *a priori*. However, because the line is so favourable experimentally it is the most suitable line for the study of rare and radioactive nuclei, as in the program of the Karlsruhe group. It is thus important to obtain values for the electronic factors in $\lambda 553.5 \text{ nm}$, and the present work was undertaken with this aim. The point is that there exist measurements (Fischer *et al.* 1974) for $\lambda 493.5 \text{ nm}$ of $\text{Ba II } (6s {}^2\text{S}_{\frac{1}{2}} - 6p {}^2\text{P}_{\frac{1}{2}})$, a line for which it is expected that the electronic factors may be calculated more reliably since it is an alkali-like transition. Our results can be combined with those in $\lambda 493.4 \text{ nm}$ by means of a King plot (King 1963) to give simple relations between the electronic factors in the two lines. Thus, the electronic data for $\lambda 493.4 \text{ nm}$ can be used in extracting nuclear information from measurements in $\lambda 553.5 \text{ nm}$.

We note that it is quite possible that in the future the calculations even for $\lambda 493.4 \text{ nm}$ will be shown to be significantly in error. Nevertheless, the importance of the present results and of the King plot remains, in that calculations carried out for either transition may be used to interpret shifts measured in both. It is also important to be able to relate shifts in different lines when comparing optical results with those from other types of experiments (muonic and electronic X-ray isotope shifts and electron scattering). As shown below, these experiments allow some normalization of the optical data, and should eventually permit the electronic calculations to be bypassed altogether.

In what follows we use the nomenclature and sign convention of Brimicombe *et al.* (1976), except for the use of frequency ν rather than wavenumber σ . Let $\nu_{i,A}$ be the frequency of the component due to an even isotope (or the centre of

gravity of an odd isotope) of mass number A in a spectral line λ_i of barium; $i = 1, 2$ refers to $\lambda\lambda 553.5, 493.4$ nm respectively. Then $\delta\nu_{i,AA'} = \nu_{i,A} - \nu_{i,A'}$ is the isotope shift, which can be written as the sum of a 'field' and a 'mass' shift as follows:

$$\delta\nu_{i,AA'} = \beta_i P_i \delta\langle r^2 \rangle_{AA'} + M_i \left(\frac{A - A'}{2} \right) \frac{136 \times 138}{A \times A'}. \quad (7)$$

In this expression $\delta\langle r^2 \rangle_{AA'}$ is the difference between the mean square radii of the nuclear charge distributions, and β_i, P_i and M_i are quantities which depend on the electronic structure of the levels of the transition. We discuss these quantities in turn.

P_i is proportional to the difference in probability density of the optical electrons at the nucleus from one level to the other; it is negative for both transitions since in each there is one more s -electron in the lower than in the upper level. β_i is a scaling factor to include the effects of core electrons. Fischer *et al.* (1974) give the results of semi-empirical and Hartree-Fock calculations from which one finds $\beta_2 P_2 = -4980$ MHz fm⁻² (with $\delta\nu_{i,AA'}$ in MHz and $\delta\langle r^2 \rangle_{AA'}$ in fm²). Although they make no estimate of error, it is usual to assume that for an alkali-like transition of this type the uncertainty is of the order of a few parts per cent.

M_i is the mass shift, the usual sum of 'normal' and 'specific' contributions N_i and S_i respectively, between the arbitrarily chosen pair of isotopes with $A = 138, A' = 136$. The normal mass shift can be calculated easily: we have $N_1 = 31.45$ MHz, $N_2 = 35.26$ MHz. Calculations and experimental comparisons in a range of elements have suggested that specific mass shifts in transitions of the types ns - np and ns^2 - $nsnp$ have magnitudes of the order of or less than the corresponding normal shifts (Edwin & King 1969). Explicit calculation gives $S_2 = -44.4$ MHz (Fischer *et al.* 1974).

We now use a King plot to relate $\beta_1 P_1$ and M_1 to $\beta_2 P_2$ and M_2 . Eliminating $\delta\langle r^2 \rangle_{AA'}$ from the two equations (7), we obtain

$$f(AA') \delta\nu_{1,AA'} = (\beta_1 P_1 / \beta_2 P_2) f(AA') \delta\nu_{2,AA'} + \{M_1 - (\beta_1 P_1 / \beta_2 P_2) M_2\}, \quad (8)$$

where
$$f(AA') = \frac{2}{A - A'} \frac{A \times A'}{136 \times 138}.$$

We shall refer to the quantities $\beta_1 P_1 / \beta_2 P_2$ and $M_1 - (\beta_1 P_1 / \beta_2 P_2) M_2$ as the King parameters ϕ and ρ ; they are respectively the slope and intercept of the plot for $f(AA') \delta\nu_{1,AA'}$ against $f(AA') \delta\nu_{2,AA'}$. In evaluating these quantities we have used our own data, those of the Karlsruhe group and a compilation of results (some unpublished) from the Marburg group. The consistency of the results for the two lines is excellent.

We find
$$\phi = 0.822 \pm 0.027,$$

$$\rho = 23.4 \pm 2.8 \text{ MHz.}$$

These results are of course independent of any assumptions concerning $\beta_i P_i$ or M_i . We note that ϕ is significantly higher than the values of around 0.6 obtained from

screening estimates or Hartree–Fock calculations (Bauche & Champeau 1976). We find also that setting $S_2 = -44.4$ MHz in the numerical relation $S_1 = 20.9 + 0.822S_2$ MHz gives $S_1 = -15.5$ MHz.

This analysis shows that the shifts $\delta\nu_{1,AA'}$ and $\delta\nu_{2,AA'}$ will yield the same values for $\delta\langle r^2 \rangle_{AA'}$ provided that the electronic factors are chosen to give the above values for ϕ and ρ . In terms of $\beta_2 P_2$ and S_2 , equation (7) may be written

$$\delta\langle r^2 \rangle_{AA'} = \frac{1}{\beta_2 P_2} \left\{ \delta\nu_{2,AA'} - \frac{(35.26 + S_2)}{f(AA')} \right\}, \quad (9a)$$

or

$$\delta\langle r^2 \rangle_{AA'} = \frac{1}{\phi\beta_2 P_2} \left\{ \delta\nu_{1,AA'} - \frac{\rho + \phi(35.26 + S_2)}{f(AA')} \right\}. \quad (9b)$$

TABLE 2. ISOTOPE SHIFTS IN $\lambda 553.5$ nm OF Ba I

isotope pair mass numbers		measured isotope shift/MHz	$\delta\langle r^2 \rangle/\text{fm}^2$
A	A'		
138	137	-214.7 (5)	0.067
138	136	-127.5 (13)	0.061
138	135	-258.7 (7)	0.108
138	134	-142.8 (12)	0.095

The values of $\delta\langle r^2 \rangle$ were derived by combining the present results with other optical data and with muonic and electronic X-ray measurements; S_1 is taken as 89.5 MHz (see text).

To derive explicit values of $\delta\langle r^2 \rangle$ from the measured isotope shifts, it thus remains to choose explicit values for $\beta_2 P_2$ and S_2 . Those already quoted give results in very poor agreement with data from muonic and X-ray isotope shift measurements (see table 3). Because of the consistency of the values obtained by these methods for $\delta\langle r^2 \rangle_{138,136}$, we choose $\beta_2 P_2$ and S_2 so that the result from the optical measurements is consistent also. We achieve this by adjusting S_2 , since this is expected to be the least reliably known of the electronic factors. We obtain $S_2 = 83.4$ MHz (the corresponding value of S_1 is 89.5 MHz), and values of $\delta\langle r^2 \rangle_{AA'}$ for isotopes studied in the present work as shown in column 3 of table 2.

An alternative procedure would be to allow $\beta_2 P_2$ to vary also, and thus to bring the optical and other data into as good agreement as possible over all isotope pairs. We do not do so, for the following reasons.

(i) With $\beta_2 P_2$ fixed at -4980 MHz fm^{-2} and $S_2 = 83.4$ MHz there is consistency between the optical and muonic data for $\delta\langle r^2 \rangle_{137,136}$. While this is satisfactory, it must be remembered that muonic odd-even shifts are subject to corrections of uncertain magnitude before they can be directly compared with optical measurements.

(ii) The X-ray and optical data cannot be brought into agreement whatever the values of the electronic factors. It can easily be shown that one of the odd-even X-ray shifts at least must be grossly in error, by taking the difference $\Delta = \delta\langle r^2 \rangle_{137,136} - \delta\langle r^2 \rangle_{135,134}$ as found from the optical and X-ray measurements. Uncertainties

due to mass shifts in both types of experiment are then almost totally absent in Δ ; even allowing a 20% error in $\beta_2 P_2$ we find $\Delta(\text{opt.}) = 0.007 \pm 0.001 \text{ fm}^2$, to be compared with $\Delta(\text{X-ray}) = 0.039 \pm 0.026 \text{ fm}^2$.

The values of $\delta\langle r^2 \rangle$ in table 2 are not consistent with those quoted by the Karlsruhe group, who have chosen to assume $S_2 = 0$. This assumption gives $S_1 = 20.9 \text{ MHz}$ and leads to values of $\delta\langle r^2 \rangle$ shown in the last column of table 3. We consider that normalization to muonic data is a more acceptable procedure, but recognize that the choice of a value of S_2 remains a major source of uncertainty.

TABLE 3. VALUES OF $\delta\langle r^2 \rangle$ FOR THE ISOTOPES OF BARIUM

		$\delta\langle r^2 \rangle_{A,A'}/\text{fm}^2$			
		optical ^c			
mass numbers		electronic	$S_1 = 89.5$	$S_1 = -15.5$	$S_1 = 20.9$
$A-A'$	muonic atoms ^a	X-ray ^b	MHz	MHz	MHz
138-136	0.062 (5)	0.057 (13)	0.061	0.035	0.044
137-136	0.002 (12)	-0.001 (13)	-0.006	-0.019	-0.015
136-134		-0.022 (13)	0.034	0.008	0.017
135-134		-0.040 (13)	-0.013	-0.026	-0.022

^a Thompson (1969); ^b Sumbaev *et al.* (1969); ^c This work.

Comparison of optical with muonic and electronic X-ray data for three assumed values of the specific mass shifts S_1 between ^{138}Ba and ^{136}Ba in $\lambda 553.5 \text{ nm}$. $S_1 = 89.5 \text{ MHz}$ (column 4) gives consistency with muonic measurements; $S_1 = -15.5 \text{ MHz}$ (column 5) is a theoretically based value; $S_1 = 20.9 \text{ MHz}$ (column 6) corresponds to $S_2 = 0$.

The results for the chain of twelve barium isotopes now obtainable show interesting trends which are discussed by Nowicki *et al.* (1978) in the light of the theoretical work available. Fischer *et al.* (1974) compare $\delta\langle r^2 \rangle$ in barium with results for neighbouring elements. We do not embark here on a further discussion of essentially the same data since this would be repetitive. However, it is clear that measurements on long chains of nuclei with common Z are a promising method for testing nuclear models, and precise data of the kind presented here are now enabling these tests to be much more quantitative than was possible before tunable laser techniques became available.

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