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Double resonance, fluorescence spectroscopy, and hyperfine structure in Pr I

W. J. Childs and L. S. Goodman
Argonne National Laboratory, Argonne, Illinois 60439

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Laser-fluorescence spectroscopy and the laser-rf double-resonance method are combined to classify lines in the Pr I absorption spectrum. The double-resonance technique is found to be particularly valuable for this purpose since, by focusing on the lower level of a transition, it leads in many cases to unique line assignments. Precise (~ 1 ppm) measurements are reported for the hyperfine-structure (hfs) constants of 15 low levels, and 0.5% values for 34 higher levels. Classifications are given for many lines in the region $5746 < \lambda < 6148$ Å. Preliminary values are derived from the double-resonance data for the single-electron hfs integrals a_{4f}, a_{5d}, a_{6s}, b_{4f}, and b_{5d} for the low-electron configurations of Pr I.

I. INTRODUCTION

Although the spectroscopy of Pr I dates back many years, the spectrum is so dense and complex that it is only recently that much progress has been made toward the systematic classification of levels. Much of this recent progress has been the result of work by Blaise, Verges, Wyart, Camus, and Zalubas[1] and by Blaise and Ginibre[2]; and much is still unpublished. The National Bureau of Standards (NBS) summarized the known lines, with classifications where available, in 1975,[3] and the known levels in 1978.[4] A 1976 review article by Blaise[5] gives much additional information. A study of these publications immediately establishes the extreme complexity of the spectrum. A number of configurations of both parities lie low, and there are nearly 40 levels below 10 000 cm^{-1}.

The hyperfine structure (hfs) of the ground $4f^3 6s^2\,{}^4\mathrm{I}$ multiplet was first studied in 1953 by Lew[6] using the atomic-beam magnetic-resonance technique, and Böklen *et al.*[7] in 1975 used the same method, but with the Ramsey[8] separated field technique, to measure the ground-state hfs to extremely high precision.

The original motivation for the present work was the achievement of a unified understanding of the hfs of the many acessible low levels in terms of a small number of radial integrals which could then be compared with *ab initio* values. Although achievement of this original goal is still in the future, many other interesting results have been obtained in the meantime. One of the more interesting results of the work has been the finding that the double-resonance technique can be extremely useful for the classification of spectral lines. Although this finding is the theme of the present report, the large body of numerical data and line classifications found is also reported.

II. METHOD

The atomic-beam, laser-rf, double-resonance technique, first developed by Rosner, Gaily, and Holt[9] in 1975 and independently by Ertmer and Hofer[10] in 1976, has been described many times. Briefly, the beam from a single-frequency, tunable, dye laser is split into a "pump" beam and a much weaker "probe" beam. The laser is tuned to be resonant with a single hyperfine component of of an optical Pr I line, and the pump beam is allowed to intersect a collimated Pr atomic beam orthogonally. The population of the particular hyperfine level of the lower state of the optical line is thereby relatively depleted, and the probe beam, which intersects the Pr beam further from its source, can therefore excite little fluorescence unless the depleted lower level can be repopulated in the space between the two laser interaction regions. This is achieved by inducing a radio frequency transition to the depleted level from a neighboring level in the lower state. The linewidth [full width at half maximum (FWHM)] of the radio frequency transitions is typically 10–40 kHz.

The identification of the different hyperfine components of the optical line to be studied should be known before the double-resonance technique is applied. This is easily achieved with the same apparatus. If the pump beam is blocked and the fluorescence excited in the atomic beam by the laser probe beam is recorded as the laser wavelength is scanned through a line, the resulting spectrum is virtually Doppler-free and the hfs components are well resolved. Analysis of their spacings and relative intensities then leads to their identification.

III. APPARATUS

The experimental setup used for the present work has been described previously.[11] The Pr atomic beam is produced by electron-bombardment heating of a 1.7-cm long, 0.8-cm-diameter tantalum oven containing a charge of Pr metal. Atoms that emerge from the 1-mm-diameter orifice of the oven are collimated to form the atomic beam. About 100 W are needed for a reasonable beam intensity.

The dye laser was Coherent Radiation CR-599-21 pumped by a Cr-12 argon-ion laser. During laser-fluorescence scans, some of the laser light was passed through a confocal, 300-MHz free-spectral-range Fabry-Perot interferometer, and the finges produced were recorded on the same strip chart as the fluorescence intensity excited in the Pr beam by the laser. The resulting incremental frequency markers (at 300-MHz intervals) were used to obtain quantitative measurement of the separation of the hfs components in the optical lines.

The laser wavelength was determined by a 0.5-m monochromator in the early stages of the experiment, and by a double Michelson interferometer, hereafter called the "λ meter," in the later stages. With the λ meter, the dye laser wavelength was measured by comparing it with a He-Ne 6328-Å standard using fringe-counting techniques.

The radio frequency power was derived from synthesizers and other equipment locked to a highly stable, 10-MHz crystal that had been calibrated against the 1771.6261-MHz hyperfine interval[12] of the electronic ground state of ^{23}Na.

IV. PROCEDURE

In the early stages of the experiment, known lines were sought by setting the laser wavelength as well as possible with the monochromator and then very slowly sweeping the laser until fluorescence was observed. Because of the enormous density of lines in the visible spectrum, however, the first line found in this way was often not the one sought. The situation was much improved toward the end of the work when (a) the availability of the λ meter made it possible to set the laser wavelength to ±0.01 Å, and (b) unpublished lists of newly classified lines were received from Blaise and Ginibre.[2]

The first step in the study of a line was to obtain a Doppler-free fluorescence spectrum as described above. Figure 1 shows a typical example, $\lambda = 5874.72$. The six strongest hfs components (FWHM$\cong$5 MHz) arise from the $\Delta F = 0$ transitions, and reflect the fact that the nuclear spin I (^{141}Pr) is 5/2. In addition, eight of the ten off-diagonal transitions are shown; the others lie to the blue (left) of the region scanned. The Fabry-Perot fringes, spaced 300-MHz apart, are shown at the top, and as tick marks below the figure. Precise measurements of the spacings of the lines, together with the standard theory of optical hyperfine structure, leads directly to the values of the electronic angular momentum J in upper and lower states, and to values (accuracy ~0.5%) of the associated magnetic-dipole hfs constants A in the two states. Although there can sometimes be an uncertainty as to which of the two states is the lower, this ambiguity can be removed by the

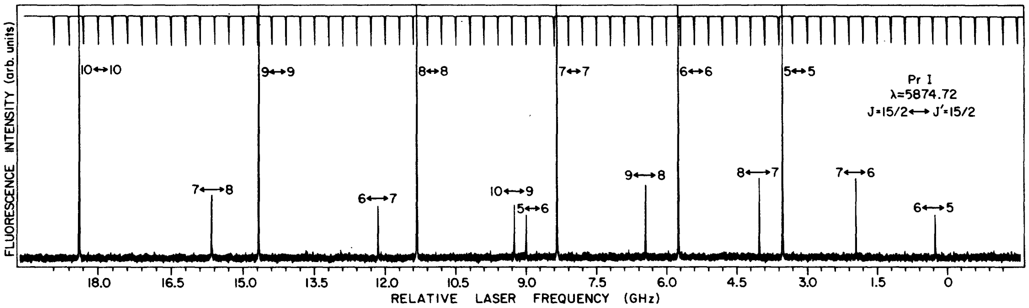

FIG. 1. Typical Doppler-free laser-fluorescence spectrum of a Pr I absorption line $\lambda = 5874.72$. The FWHM is about 5 MHz. All but two of the hfs components are included in the region scanned. Fringes from a 300-MHz free-spectral-range Fabry-Perot provide an incremental frequency scale. The F values of the components (lower-state value at the left) are given. As discussed in the text, the laser-rf double-resonance technique is used to measure the separations between selected hfs components of such optical lines to the order of 1 ppm. For example, to measure the $F = 8 \longleftrightarrow 7$ hfs interval in the lower $J = 15/2$ level of this optical line with the double-resonance technique, one would hold the laser on either of the strong $8 \longleftrightarrow 8$ or $7 \longleftrightarrow 7$ hfs components and sweep the rf slightly in the appropriate region (4334 MHz). In this figure, this corresponds to measuring the separation of the componenet $7 \longleftrightarrow 8$ from $8 \longleftrightarrow 8$ or the identical separation $7 \longleftrightarrow 7$ from $8 \longleftrightarrow 7$. These separations can be measured to ± 5 MHz from laser scans such as this one, or to ± 1 kHz by double resonance.

double-resonance technique in all cases.

Because the electric-quadrupole moment of the ^{141}Pr nucleus is extremely small[13] ($Q \cong -0.06 \times 10^{-24}$ cm^2), the electric-quadrupole hfs constant B is very small compared to the dipole constant A, and little information on the B values of the upper and lower states can be determined from the laser scans. This limitation is also overcome by application of the double-resonance technique.

The laser-rf, double-resonance technique has been described in general terms above. When applying it to a particular optical line, the procedure is to select an hfs component appropriate to the particular lower-state hfs interval to be measured, and to hold the laser wavelength at that value. The frequency of the rf field applied between the two laser interaction regions is then swept through the appropriate region and any increase in fluorescence intensity noted. The rf sweep is computer driven, and can be repeated many time while the fluorescence intensity data are accumulated. The hfs intervals measured in this way are necessarily those of the lower of the two states of the optical line (the lifetime of the upper state of an allowed transition is much shorter than the ~1-ms transit time of the atom in the apparatus). The measured hfs intervals, on analysis, lead immediately to precise values for the dipole and quadrupole hfs constants A and B and the J value for the lower state of the transition.

Because the lower-state hfs intervals are routinely measured to 1 or 2 kHz (typically 1 ppm or better), they serve as excellent identification labels for the lower level of an optical transition. Thus if two optical lines have lower levels of equal J and in addition the fluorescence scans indicate equal A values, the double-resonance technique can be used to measure one or more hfs intervals in the lower level of each transition precisely. If they are the same to the 1 ppm or better experimental precision, it is established (to a very high order of probability) that the two optical lines do indeed have a common lower level. Figure 2 shows an example of this. The transitions $\lambda = 5821.36$, 5820.76, and 6118.02 were shown by individual fluorescence scans to have lower levels with $J = 9/2$. The double-resonance curves (Fig. 2) show the increase in fluorescence intensity as the rf was swept through the $F = 7 \longleftarrow 6$ hfs interval with the laser set on the appropriate hfs optical component for each of the three optical lines. The evidence that all three lines have a common lower level is overwhelming. The actual identification of the common $J = 9/2$ lower level is established by noting that the transition energy and upper- and lower-state J values of $\lambda = 6118.02$ are consistent with the known[4] levels 8250.22 cm^{-1} (9/2, –) and 24 590.84 cm^{-1} (11/2, +); this classification is in agreement with unpublished work of Blaise and Ginibre.[2]

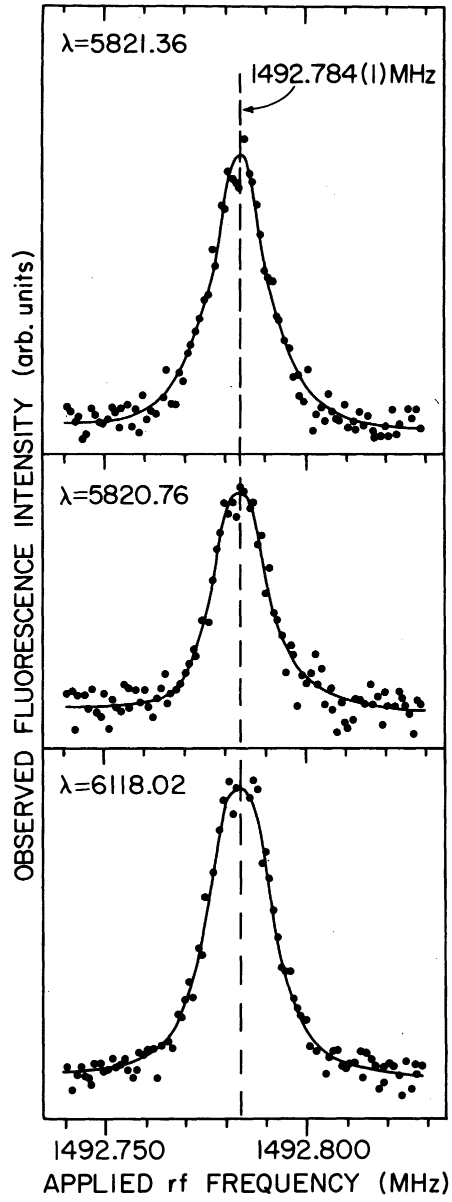

FIG. 2. Laser-rf double-resonance scans through the $F = 7 \longleftrightarrow 6$ hyperfine interval of the 8250.22 cm^{-1} (9/2, –) common lower level of three optical lines of Pr I. The identity of the observed resonance frequencies, each measured with the laser on a different optical line, establishes that the three lines do indeed have the specified common lower level. Other examples of the use of the double-resonance technique for classification of Pr I lines are discussed in the text.

V. RESULTS

Several specific examples of the usefulness of the double-resonance technique for the classification of lines will be given. The line $\lambda = 5919.78$ is not included in the NBS line list[3] and was discovered accidentally while searching for another line. A laser scan through the line (similar to that of Fig. 1) showed that it is a $J = 9/2 \leftrightarrow 9/2$ transition and, in addition, indicated that the A value of the lower state is 926 ± 5 MHz, i.e., the same as that of the $4f^36s^2\,{}^4I_{9/2}$ atomic ground state to within the experimental error inherent in our laser-fluorescence measurements. Accordingly, double resonance was used to measure the $F = 7 \leftrightarrow 6$ hfs interval. The result was 6477.912 MHz, within 1 kHz of the known[7] ground-state value, thereby proving that $\lambda = 5919.78$ goes to the ground state and establishing a previously unknown 9/2, + excited level at 16 887.84 cm^{-1}.

The line $\lambda = 5915.31$, listed in the NBS compilation,[3] was studied by double resonance and the hfs intervals of its lower level were precisely measured. Subsequently, the lower level of the line $\lambda = 5956.25$, which was found accidentally and is not included in the NBS line list,[3] was found to have exactly the same $F = 8 \leftrightarrow 7$ hfs interval (4404.798 MHz). The new line, $\lambda = 5956.25$, therefore has the same lower level as $\lambda = 5915.31$. The common lower level is identified as 6892.95 cm^{-1} (11/2, +) by Blaise and Ginibre.[2]

Double resonance was also used to show that the lower levels of $\lambda = 5941.65$ and 5879.04 are the same ($J = 15/2$), and all the hfs intervals were measured. The A value is found to be 763.306 MHz. The actual identification of the level was given by Blaise and Ginibre[2]; it is 8363.91 cm^{-1} (15/2, +). Subsequent laser scans through the new line $\lambda = 5760.20$ showed that its lower level also has $J = 15/2$ and $A = 765 \pm 5$ MHz. Double resonance was then used to measure the $F = 6 \leftrightarrow 5$ hfs interval in the lower level of $\lambda = 5760.20$. It was found to be 4595.475 MHz, which is 757 ± 3 kHz (or 0.016%) larger than the 4594.718 MHz measured for the level 8363.91 cm^{-1} (15/2, +) level. This proves clearly that although the two levels have the same J value and their hyperfine intervals differ by only 0.016%, they are not the same level. The new level is probably the $J = 15/2$, + level identified by Blaise and Ginibre[2] at 8765.57 cm^{-1}.

It should be noted that the double-resonance technique (together with appropriate laser scans) is useful not only for the identification of the lower levels of previously unclassified lines, but also establishes unambiguously the existence and properties of previously unknown highly excited states. These can then be checked for transitions to other low levels in the usual way.

Table I summarizes the present double-resonance measurements of hfs intervals in Pr I. The dipole and quadrupole hfs constants A and B derived from fitting the simple theory (and ignoring higher-order effects) to these intervals are given, as are the residuals. The uncertainties in the observations are typically a few kHz. The hfs intervals for the levels of the $4f^36s^2\,{}^4I$ ground multiplet are known from previous work[6,7] and are omitted, although the hfs constants derived from them are included for completeness.

Although a detailed interpretation of the double-resonance results is not the purpose of the present report (the collection of precise hfs data for the low levels of Pr I is not yet complete), a very brief account of the present preliminary state of the interpretation can be given. As mentioned above, one of the original motivations for the Pr work was the reduction of a large number of precise experimental dipole and quadrupole hfs constants (A and B values) to a much smaller number of radial integrals that could then be compared with *ab initio* calculations. This procedure has been described in detail previously.[14] One first develops eigenvectors for all the states of interest by iteratively fitting the Hamiltonian containing the Coulomb, spin-orbit, and associated interactions to the known fine-structure energies. This is done independently for the positive- and negative-parity excited states. The two configurations $4f^25d6s^2$ and $4f^25d^26s$ were spanned simultaneously for the even-parity states, and $4f^35d6s$ for the odd-parity states. Standard expressions for the effective hyperfine interaction operators, expressed as linear combinations of the appropriate radial integrals, are then used, with the eigenvectors, to generate expectation values of the hfs constants. The expressions for the dipole constants A, after simplification, are linear in the single-electron dipole hfs parameters a_{4f}, a_{5d}, and a_{6s}. The first two of these are proportional to $\langle r^{-3}\rangle_{4f}$ and $\langle r^{-3}\rangle_{5d}$, respectively, and the third to $|\psi_{6s}(0)|^2$. The expressions for the quadrupole constants B are linear in b_{4f} and b_{5d}, which are proportional to $\langle r^{-3}\rangle_{4f}$ and $\langle r^{-3}\rangle_{5d}$, respectively.

After these expressions were obtained, they were least-squares fitted to the measured A and B values to obtain the best-fit values for the single-electron parameters a_{nl} and b_{nl}. Table II gives the results of preliminary fits to the data obtained so far. The odd- and even-parity excited levels were fitted separately, as were the levels of the ground multiplet $4f^36s^2\,{}^4\text{I}$. For the even-parity levels, it was assumed that $a_{4f}(4f^25d6s^2) = a_{4f}(4f^25d^26s)$ and $a_{5d}(4f^25d6s^2) = a_{5d}(4f^25d^26s)$

TABLE I. Summary of double-resonance observations on low levels of Pr I. The measured hfs intervals are given in column six, and the differences between these values and those calculated from the derived hfs constants in column seven. Second-order hfs corrections are not included. Columns 2 and 3 contain the derived values of the magnetic-dipole (A) and electric-quadrupole (B) hfs constants in MHz. The excitation energy, J value, and parity are given for each level in columns 1 and 4. The hfs intervals of the four lowest levels have been published previously.

Excitation energy (cm^{-1})	A (MHz)	B (MHz)	J,π	$F \leftrightarrow F'$	Observed energy interval (MHz)	Obs. − Calc. (kHz)
0.00	926.209[a,b]	−11.878[a,b]	9/2, −			
1 376.60	730.393[a]	−11.877[a]	11/2, −			
2 846.75	613.240[a]	−12.850[a]	13/2, −			
4 381.10	541.575[a]	−14.558[a]	15/2, −			
8 080.49	238.352	−22.961	11/2, −	$8 \leftrightarrow 7$	1896.801	3
				$7 \leftrightarrow 6$	1666.270	−3
				$6 \leftrightarrow 5$	1433.116	−2
				$5 \leftrightarrow 4$	1197.710	0
				$4 \leftrightarrow 3$	960.426	4
8 250.22	213.531	−4.136	9/2, −	$7 \leftrightarrow 6$	1492.784	−3
				$6 \leftrightarrow 5$	1280.879	4
				$5 \leftrightarrow 4$	1068.347	3
				$4 \leftrightarrow 3$	855.294	−2
				$3 \leftrightarrow 2$	641.831	−3
8 733.50	854.297	−31.807	13/2, −	$9 \leftrightarrow 8$	7675.458	0
				$8 \leftrightarrow 7$	6830.946	−2
				$7 \leftrightarrow 6$	5983.501	−1
				$6 \leftrightarrow 5$	5133.488	1
				$5 \leftrightarrow 4$	4281.274	4
8 835.42	949.091	−13.721	11/2, −	$8 \leftrightarrow 7$	7586.736	−1
				$7 \leftrightarrow 6$	6642.326	1
				$6 \leftrightarrow 5$	5696.342	2
				$5 \leftrightarrow 4$	4749.008	0
				$4 \leftrightarrow 3$	3800.551	−3
9 646.90	907.515	−23.132	15/2, −	$10 \leftrightarrow 9$	9065.898	6
				$9 \leftrightarrow 8$	8164.948	−10
				$8 \leftrightarrow 7$	7262.228	1
				$7 \leftrightarrow 6$	6357.921	−1
				$6 \leftrightarrow 5$	5452.229	4
9 684.24	991.907	−7.246	13/2, −	$9 \leftrightarrow 8$	8924.150	−3
				$8 \leftrightarrow 7$	7934.478	3
				$7 \leftrightarrow 6$	6944.133	4
				$6 \leftrightarrow 5$	5953.197	−1
				$5 \leftrightarrow 4$	4961.760	−4
10 669.00	951.310	−2.670	15/2, −	$10 \leftrightarrow 9$	9512.037	1
				$9 \leftrightarrow 8$	8561.484	−1
				$8 \leftrightarrow 7$	7610.726	−1
				$7 \leftrightarrow 6$	6659.784	−3
				$6 \leftrightarrow 5$	5708.690	4
4 866.54	867.997	−50.319	11/2, +	$8 \leftrightarrow 7$	6922.024	2
				$7 \leftrightarrow 6$	6071.178	−1
				$6 \leftrightarrow 5$	5214.569	−3
				$5 \leftrightarrow 4$	4353.024	−1
				$4 \leftrightarrow 3$	3487.364	4
6 603.60	755.456	−48.633	13/2, +	$9 \leftrightarrow 8$	6778.898	−1
				$8 \leftrightarrow 7$	6038.408	1
				$7 \leftrightarrow 6$	5293.426	−1
				$6 \leftrightarrow 5$	4544.518	0
				$5 \leftrightarrow 4$	3792.242	0
6 714.22	474.692	−29.633	11/2, +	$8 \leftrightarrow 7$	3784.599	−5
				$7 \leftrightarrow 6$	3320.019	5
				$6 \leftrightarrow 5$	2852.034	4

TABLE I. (*Continued*).

Excitation energy (cm^{-1})	A (MHz)	B (MHz)	J,π	$F\leftrightarrow F'$	Observed energy interval (MHz)	Obs. − Calc. (kHz)
				5↔4	2381.137	0
				4↔3	1907.812	−7
6 892.95	551.949	−24.736	11/2, +	8↔7	4404.798	−1
				7↔6	3861.277	−6
				6↔5	3314.931	−2
				5↔4	2766.156	2
				4↔3	2215.361	9
7 630.16	776.286	−43.592	13/2, +	9↔8	6968.468	−1
				8↔7	6205.596	0
				7↔6	5438.701	2
				6↔5	4668.281	1
				5↔4	3894.841	−3
8 363.91	763.306	−48.253	15/2, +	10↔9	7613.754	−1
				9↔8	6864.172	−3
				8↔7	6110.859	11
				7↔6	5354.236	−1
				6↔5	4594.718	−5
	763.557	−45.805	15/2, +[d]	10↔9	7617.252	2
				9↔8	6866.714	−8
				8↔7	6112.648	11
				7↔6	5355.432	−3
				6↔5	4595.475	−2
9 770.33[c]	905.498	−40.819	17/2, +	11↔10	9944.627	0
				10↔9	9050.028	3
				9↔8	8152.724	3
				8↔7	7252.982	−4
				7↔6	6351.086	−4

[a] Reference 6.

[b] Reference 7.

[c] Level energies from Blaise and Ginibre, Ref. 2.

[d] This $J=15/2$ level is probably the (15/2,+) level identified by Ginibre at 8765.57 cm^{-1} in Refs. 2 and 17.

TABLE II. Single-electron hfs parameter values derived from least-squares fits to the A and B values given in Table I. The values are preliminary; data must be collected for more levels before truly reliable values can be quoted. The most noteworthy result is the striking difference found for a_{5d} for the excited odd- and even-parity levels. These results are discussed and compared with new relativistic *ab initio* calculations of Cheng in the text.

Parameter	$4f^36s^2\,{}^4I$ levels (MHz)	Odd-parity excited levels $4f^35d6s$ (MHz)	Even-parity excited levels $4f^25d^26s+4f^25d6s^2$ (MHz)
a_{4f}	684	687	598
a_{5d}		251	744
a_{6s}		7921	8311
b_{4f}	−53.8	−51.4	−58.2
b_{5d}		−29.5	−39.0
a_{4f}/a_{5d}		2.74	0.80
b_{4f}/b_{5d}		1.74	1.49

for simplicity. The new electric-quadrupole results are the only data available for the excited configurations of Pr.

The point most worthy of note is the very large difference in a_{5d} for the two parities. Although the magnitude of this effect is puzzling [a_{5d}(even)/a_{5d}(odd) = 2.96 ± 1.3 experimentally], new relativistic self-consistent calculations by Cheng[15] indicate that a_{5d} should be 45–70% larger for the even-parity levels. The corresponding effect for the quadrupole interaction is the difference for b_{5d} between the two parities. The observed value of the ratio b_{5d}(even)/b_{5d}(odd) = 1.32 is much closer to Cheng's prediction.[15] The better agreement between theory and experiment for the quadrupole interaction is expected theoretically[16] because of the smaller effect of configuration interaction on quadrupole hyperfine structure. The discrepancies presumably arise from (a) the limited subset of levels for which data is available, (b) the lim-

TABLE III. Classification of 33 lines in the absorption spectrum of Pr I. The excitation energy, J value, and parity are given for each level. The dipole hfs constant A is given for the upper levels; the values for the lower levels are given in Table I except for $\lambda = 5929.49$, for which the lower-level A value is 840.2 MHz. The classifications are consistent in almost every case with independent, unpublished work of Blaise and Ginibre.

	Lower-level		Upper-level		
Wavelength (Å)	Excitation energy (cm^{-1})	J, π	Excitation energy (cm^{-1})	J, π	hfs A factor (MHz)
6148.17[a]	6714.22	11/2,+	22974.55	13/2,−	629.2
6118.02[a]	8250.22	9/2,−	24590.84	11/2,+	914.1
6055.13[a]	8080.49	11/2,−	24590.84	11/2,+	914.7
6049.26[a]	7630.16	13/2,+	24156.54	15/2,−	894.6
6008.54[a]	8835.42	11/2,−	25473.75	9/2,+	808.0
5996.06[a]	9684.24	13/2,−	26357.24	11/2,+	746.3
5991.27	9646.90	15/2,−	26333.23	15/2,+	547.9
5978.88[a]	8733.50	13/2,−	25454.41	13/2,+	775.9
5976.95	1376.60	11/2,−	18102.90	11/2,+	593.0
5963.00[a]	8733.50	13/2,−	25498.90	13/2,+	627.7
5962.18	1376.60	11/2,−	18144.32	13/2,+	524.4
5959.25	10669.00[b]	15/2,−	27444.99	13/2,+	535.0
5956.75	9770.33[b,c]	17/2,+	26553.36	15/2,−	738.0
5956.25	6892.95	11/2,+	23677.39	13/2,−	657.7
5941.65	8363.91[b]	15/2,+	25189.58	17/2,−	641.3
5929.49	12945.56[b]	19/2,−	29805.84	21/2,+	385.6
5920.76[d]	6603.60[b]	13/2,+	23488.64	15/2,−	786.4
5919.78	0.00	9/2,−	16887.84	9/2,+	652.0
5915.97[a]	7630.16	13/2,+	24528.91	15/2,−	756.9
5915.31	6892.95	11/2,+	23793.55	13/2,−	624.7
5879.11	8835.42	11/2,−	25840.18	13/2,+	654.9
5879.04	8363.91[b]	15/2,+	25368.78	17/2,−	663.1
5878.10[a]	9646.90	15/2,−	26654.48	15/2,+	534.5
5874.72[d]	4381.10	15/2,−	21398.47	15/2,+	913.0
5835.13[a]	4866.54	11/2,+	21999.38	13/2,−	976.1
5821.36	8250.22	9/2,−	25423.58	7/2,+	1198
5820.76	8250.22	9/2,−	25425.36	7/2,+	1231
5811.79	1376.60	11/2,−	18578.24	9/2,+	608.8
5792.95	9770.33[b,c]	17/2,+	27027.92	19/2,−	793.1
5792.27	1376.60	11/2,−	18636.18	9/2,+	844.7
5779.28	9770.33[b,c]	17/2,+	27068.73	19/2,−	579.5
5760.20		15/2,[e]		17/2,−[f]	771.0
5746.53	2846.75	13/2,−	20243.72	11/2,+	511.8

[a] Line correctly classified by NBS, Ref. 3.

[b] Level energy from Blaise and Ginibre, Ref. 2.

[c] Identification of lower level from Blaise and Ginibre, Ref. 2.

[d] Line incorrectly classified by NBS, Ref. 3.

[e] This $J = 15/2$ level is probably the (15/2,+) level at 8765.57 cm^{-1} identified by Ginibre (Refs. 2 and 17).

[f] If the lower level of $\lambda = 5760.20$ is that mentioned in note e, the upper (17/2,−) level is at 26121.26 cm^{-1}.

ited space spanned by the eigenvectors, and (c) simplifications applied to the hfs interactions to reduce the number of free parameters. Distortions of the hfs intervals by hyperfine interactions between different fine-structure states (i.e., second-order or off-diagonal hfs interactions) have been evaluated and do not appear to be a major factor. Collection of data for additional states will eventually lead to reduction of any systematic errors due to (a) and (c). The other empirical parameter values listed in Table II are in reasonable agreement with Cheng's *ab initio* calculations.[15]

Table III summarizes the information gained during the present work on classification of optical lines and on upper-state hfs. The dipole hfs constants A given in the final column are those determined from the laser-fluorescence spectra;

the uncertainty is about 0.5%. The hfs constants for the lower levels are given in Table I for every line except $\lambda = 5929.49$, for which double resonance has not yet been used. The A value found by laser-fluorescence spectroscopy for the 12 945.56 cm^{-1} (19/2, –) lower level of this line is 840.2 MHz. The designation a after a wavelength indicates that the line is correctly classified in Ref. 3. The superscript b indicates that while the hfs constants, J values, and wavelength of the line were measured, the actual identification of the lower level is from Blaise and Ginibre.[2] The superscript c indicates that the lower-state excitation energy is from unpublished work of Blaise and Ginibre.[2] The superscript d indicates that a line is incorrectly classified in Ref. 3 (the possibility of a very weak component with the classification of Ref. 3 cannot be excluded). The line classifications of Table III are consistent in almost every case with independent, unpublished work of Blaise and Ginibre.[2,17]

VI. CONCLUSIONS

It is clear from the resolution shown in Fig. 1 (FWHM$\cong$5 MHz) that Doppler-free laser-fluorescence spectroscopy is capable of yielding the hfs constants and J values of an optical line with much less ambiguity than the traditional lower resolution techniques. On the other hand, it cannot be easily applied to the many thousands of lines routinely studied by the traditional methods. These observations are even truer for the laser-rf double-resonance technique used in the present work. It has been demonstrated, however, that the double resonance technique is an extremely powerful method for detailed study and classification of selected lines of interest. In addition to its very high precision, it focuses on one level (the lower one) of a transition and thereby breaks the correlation inherent in most other techniques and often leads to a positive level identification. For Pr I, the resolution it affords is essential for learning anything about the electric-quadrupole hyperfine structure because of its very small size. The determination of truly reliable hfs single-electron parameter values for the low configurations of Pr I must await collection of data on additional levels.

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