Atom and Molecular Spectroscopy Laboratory report

High Resolution Laser Spectroscopy

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1 Introduction

In Physics, we are generally interested in studying how electromagnetic fields interacts with different states of matter. In general absorption is a powerful tool to study gases and liquids, gases have a sharper absorption spectrum than a liquid, thus they are more commonly studied using absorption techniques. An other useful technique when studying matter is fluorescence detection, where again it is more commonly used on gases. Absorption spectroscopy as its name implies is a technique where we illuminate a sample with a light source that we can modulate its wave length and measure the transmitted light which gives us the information of what wavelengths were absorbed. Fluorescence spectroscopy requires the same execution but instead of detecting the transmuted light we set a the detector to the side of the sample and measure the light that is being emitted by the sample, which is being produce by the emission of the the exited states, produced by the light source, going to the ground state.

In general absorption and fluorescence spectroscopy are implemented throughout different industries where they are interested in measuring in most case concentrations of different gases, as discussed in a previous laboratory session. There exists a limitation in resolution to this technique, if one is interested in executing measurements of high resolution the statistical fluctuations of the system have to be taken into account. In this experiment, we are going to implement a technique know as High Resolution Laser Spectroscopy which allows use to over pass the Doppler limit by measuring a Doppler free spectra. In are particular interest, we need very high resolution to measure fundamental quantities related to structure of molecules or atoms, are objective is to study the hyperfine components of iodine molecule and sodium atom. This was accomplished by using modern optical equipment to scan over several spectral lines by tuning the light source to the corresponding excitation frequencies of the different samples acquiring a Doppler free spectra.

2 Theory

As previously discussed we are going to use a a high resolution spectroscopy to study a set of samples, where we want to measure the hyperfine structure for different molecules. The hyperfine structure was discovered by A. Michelson, Ch. Fabry and A. Pérot at the end of the 19th century. They explained the splitting effect of the electronic levels by taking into account the interaction of the nuclear and magnetic moments interacting with the electronic shell. One can study the splitting effect by looking separately at the magnetic hyperfine structures and the electric hyper fine structure. First lets consider the magnetic hyperfine structure[1], it is associated with the spin angular momentum $\mathbf{I}$, a nucleus has a dipole moment μ_I given by :

$$\mu_I = g_I \mu_N \mathbf{I} \,. \tag{1}$$

Where μ_{N} is the nuclear magneton and g_I is a constant of proportionality that can have positive or negative sing. Now if we consider what magnetic field is produced by the electron shell felt by the nucleus $\mathbf{B}_J$ which is directed along the atomic axis of rotation $\mathbf{J}$,

$$\mathbf{B_J} = k\mathbf{J} \,. \tag{2}$$

This effect will produce a magnetic coupling between the nucleus and the electron shell, and the interaction is described by:

$$H_{\text{mhfs}} = a\mathbf{I} \cdot \mathbf{J} \,, \tag{3}$$

where a is the magnetic dipole interaction constant

$$a = -kg_I\mu_N \,. \tag{4}$$

As one can see a is a product of a nuclear quantity g_I, which is proportional to the moment, and an electronic quantity k, which is proportional to the internal magnetic field strength. With this we can measure the energy contribution for the magnetic hyperfine structure:

$$E_{\text{mhfs}} = \frac{a}{2}\left[F(F+1) - I(I+1) - J(J+1)\right] \,. \tag{5}$$

We can apply the Landé interval rule giving of a change in energy:

$$\Delta E_{\text{mhfs}(F,F-1)} = aF \,. \tag{6}$$

With this we can find the the magnetic dipole interaction constant if we can know the transition and the energy required to do drive it.

Now if we have a non-spherically symmetric charge distribution the molecule will acquire a orientational energy in a electric field gradient. The differential interaction of the nuclear structure and the variation if the field across its finite extension is much smaller than monopole interaction of the charged nucleus. The energy contribution depends on the direction of the nuclear spin in relation to the electric field gradient, giving an electric hyperfine interaction as :

$$E_{\text{ehfs}} = b\frac{(3C/4)(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)} \tag{7}$$

with

$$C = F(F+1) - I(I+1) - J(J+1) \text{ and } \; b = \frac{e^2}{4\pi\epsilon_0}q_J Q \,, \tag{8}$$

where b is an analogy to the magnetic dipole interaction constant a and its known as the electric quadrupole interaction constant b, which is a product of a nuclear quantity Q, the electric quadrupole moment and an electronic quantity q_J which is proportional to the electric field gradient. The electric hyperfine structure is of the same order of magnitude as the magnetic one, but generally a bit smaller.[1]

Its also worth mentioning that if the nucleus has no spin $I = 0$, there is neither a magnetic nor an electric hyperfine structure. For $I = 1/2$ only magnetic interaction is possible. For electrical hyperfine structure it is required $I \geq 1$ and $J \geq 1$.

3 Method

3.1 Experimental Setup

To study possible transitions between electric hyperfine levels of iodine and sodium, we used an experimental setup for high resolution laser spectroscopy, drawn on fig. 1. It comprises the following components [2]:

1. A dye laser of variable wavelength and adjustable resonator cavity length, aiming to probe sodium and iodine atoms; it operated in pulse mode at a pulse frequency of 10 Hz;
2. A Nd:YVO_4 solid-state laser (of wavelength $\lambda_p = 532\,\text{nm}$ and approximate power $P_p = 6\,\text{W}$), intended for pumping the dye laser and maintaining its lasing;
3. A wave-meter for monitoring the dye laser's wavelength, coupled to an attenuator to prevent exposing the wave-meter to excessive laser intensities;
4. A Fabry-Pérot interferometer (FPI) of cavity length $L = 75\,\text{cm}$ and whose corresponding free spectral range (FSR) is 200 MHz; its function was to properly scale spectral lines and frequency components in sodium's and iodine's respective spectra, and to measure the probe's wavelength;
5. A temperature-controlled glass cell, containing either element in a controlled environment;
6. An acousto-optic modulator (AOM) of modulation frequency N;
7. A lock-in amplifier tuned to a varying signal of frequency N.

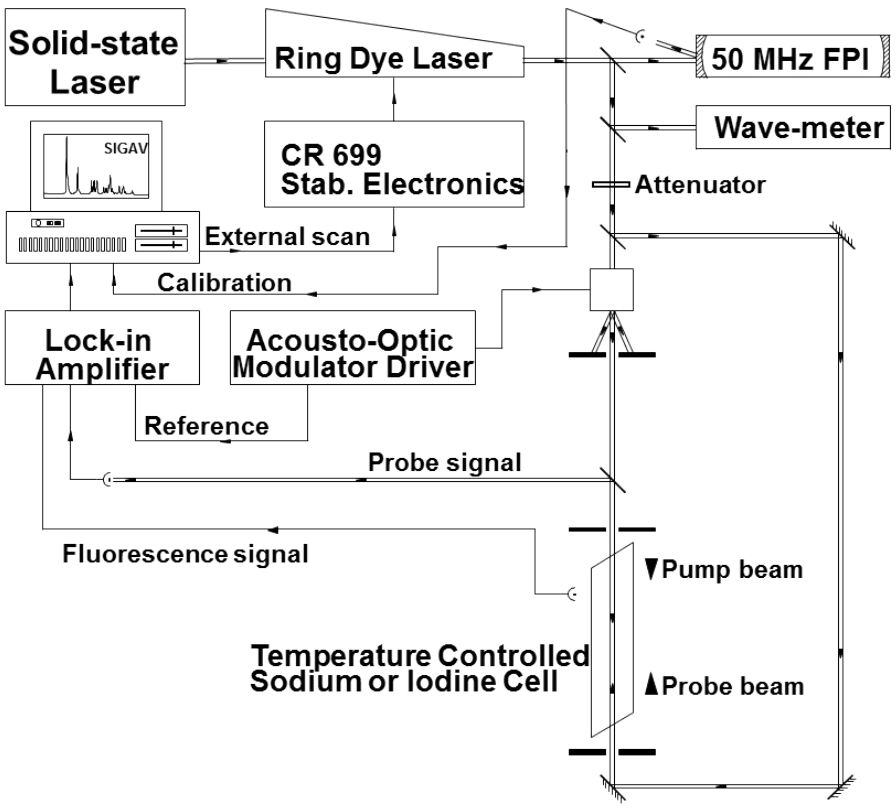


Figure 1: Experimental setup used for high resolution laser spectroscopy. Illustration taken from [2].

The first three components create a pump and probe beam, directed onto iodine or sodium. In particular, since the pump (solid-state) laser was strong enough to be able to saturate the probe's transition, the pump's intensity was monitored in order to avoid a saturation that would subsequently broaden spectral lines. Additionally, the dye laser's cavity was finely tuned to output a

wavelength as close as possible from the target one λ_d (monitered using the wave-meter)

Signal detection was achieved using the AOM and the lock-in amplifier. Through standing sound waves in its crystal, the AOM separates incoming light of frequency ν into several beams of different frequencies $\nu' = \nu + pN$ (with p an integer) and different diffraction angles.

Atoms in the glass cell were not stationary; they were characterized by a distribution of velocities in all directions of space. For instance, at too high pressures in the gas cell, atom-atom collisions could occur and eventually result in pressure induced line broadening [1, sec. 7.4]. Additionally, atoms moving along the same axis as the probe beam would perceive a perceive a different wavelength than its actual one due to Doppler effect. Energy levels may therefore be shifted, allowing photons from the probe beam to be absorbed by virtual levels at different energies than with atoms at rest. These virtual levels would eventually influence the appearance of spectral lines, depending on allowed transitions and on the probe beam's wavelength.

3.2 Measurement Methods

Inside the AOM, sound waves are repetitively turned on and off by a pulse generator at frequency f. In a similar fashion than with wavelength modulation spectroscopy, the aim of such scheme was to reduce signal noise: the probe's wavelength would be modulated by a reference signal at a frequency f (with a relative phase shift ϕ), with the signal obtained after transmission through the gas cell would be evaluated either at this frequency or one of its harmonics. This signal would contain a zero-frequency level component, and one at higher frequencies which could be filtered to only retain the zero-frequency level component. Since noise fluctuations educed through modulation are proportional to $1/f$, the laser was modulated at a higher Fourier-frequencies f than DC. The higher f was, the lower fluctuations were, and the better the resulting signal-to-noise ratio was [3]. For measurements with both sodium and iodine, we tuned the relative phase shift ϕ in order to optimize the subsequent signal and increasing the signal-to-noise ratio [4]. The FSR and the signal coming from the lock-in amplifier were recorded by a custom LabVIEW program, which also analyzed and curve-fitted the measured spectrum.

Probe wavelength for sodium For spectral measurements with sodium, the dye laser's wavelength was adjusted to $\lambda = 589.598\,\text{nm}$ by adjusting its cavity length. The aim was to correspond the D_1 transition line of sodium, which corresponds to the transition between the states $3\,^2S_{1/2}$ and $3\,^2P_{1/2}$, and results in a line at approximately at 590 nm.

Probe adjustment for iodine In the same manner for iodine, and in order to prevent line broadening from saturation, the probe's wavelength was also adjusted to a wavelength (576.1351 nm) as close as possible to that of iodine's P(62)17-1 transition line in air (576.1343 nm) by adjusting the dye laser's cavity length. An illustration of sub-optimal spectrum is shown on fig. 2; this spectrum deviates from a Gaussian shape (which could have been expected from a non-zero linewidth caused by the limited lifetimes of iodine's energy levels) by a slight dip. This example illustrates how the expected 15 transitions were broadened enough by saturation to overlap each other, forming a band itself that could not be resolved–hence why the probe's wavelength was adjusted.

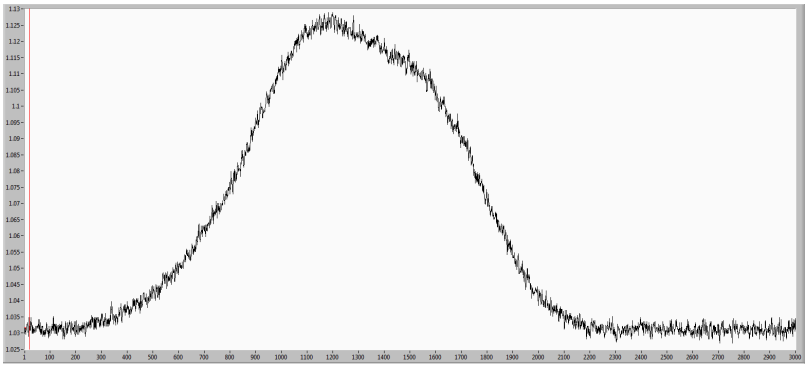


Figure 2: Illustration of the shape of iodine's hyperfine spectrum around the transition line P(62)17-1 when broadening occurs as a result of saturation from the probe beam. This line does not display a shape that could be approximated as Gaussian or Lorentzian without visible deviations. Units are arbitrary.

4 Result

4.1 Evaluation of hyperfine iodine spectrum

A spectrum of the hyperfine structure of iodine has been taken. The transition is known as the P(62)17-1 line. According to figure 3, 15 peaks can be observed in the spectrum.

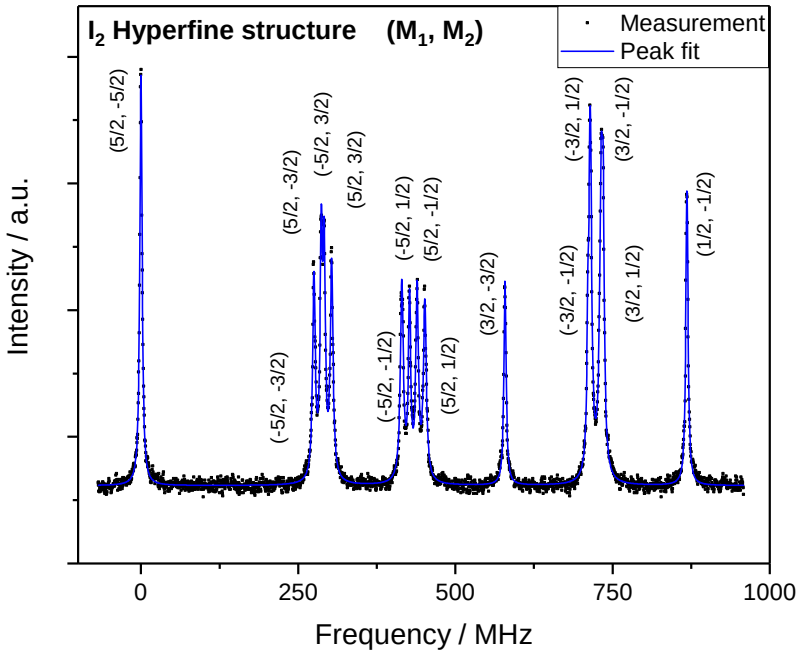


Figure 3: Iodine hyperfine spectrum for the P(62) 17-1 transition.

The peaks were fit with a Lorentz-profile which determines the central position of the peak as well as the FWHM. The values can be found in table 1.

Table 1: Frequencies and the according M_1/ M_2 values observed in the Iodine spectrum. The grey values have a worse agreement to the calculated line positions and should not be used for the calculations.

(M_1,M_2)	Frequency MHz	FWHM MHz
(5/2,-5/2)	0.000	4.396
(-5/2,-3/2)	275.075	5.025
(5/2,-3/2)	286.741	4.446
(-5/2,3/2)	291.421	4.517
(5/2,3/2)	303.246	5.187
(-5/2,-1/2)	414.877	5.723
(-5/2,1/2)	427.104	4.406
(5/2,-1/2)	439.133	5.011
(5/2,1/2)	451.463	5.557
(3/2,-3/2)	578.977	4.263
(-3/2,-1/2)	710.686	3.145
(-3/2,1/2)	714.491	5.294
(3/2,-1/2)	731.932	5.999
(3/2,1/2)	735.079	4.086
(1/2,-1/2)	868.235	4.210

The Energy for the hyperfine structure E_{hfs} is given with [2]:

$$E_{hfs} = \sum_{n=1}^{2} \left\{ a/_2 C_n + b \frac{3/4 C_n \left(C_n + 1\right) - I_n \left(I_n + 1\right) J(J+1)}{2 I_n \left(2 I_n - 1\right) J(2J-1)} \right\} \tag{9}$$

Nucleus	n	**Nuclear spin**	I_n
Rotational quantum number	J		

While C_n is:

$$C_n = F_n \left(F_n + 1\right) - I_n \left(I_n + 1\right) - J(J+1) \tag{10}$$

Furthermore, F_n is the total angular momentum:

$$\mathrm{F_n} = \mathrm{J} + \mathrm{I_n} \tag{11}$$

For large J, F can be approximated with:

$$\mathrm{F_n} \approx \mathrm{M_n} + \mathrm{J} \tag{12}$$

We observe in the spectra of iodine (figure 3) and tabular 1 the given transitions:

$$(\mathrm{F_1},\mathrm{F_2}) = (\mathrm{M_1} + \mathrm{J},\mathrm{M_2} + \mathrm{J}) \tag{13}$$

Since we know that we observed the P(62)17-1 line, this means the transition from (v'=17,J'=61) to (v"=1,J"=62) in $^{127}I_2$. J' is the upper state, therefore the momentum the upper state is J = 61. We observe the transitions of the third group of measurement. To obtain the values of Δ a and Δ b we first need to calculate the C_n values:

Table 2: Values taken from table 1 for the evaluation of the measurement as well as the results for the C_n and F_n.

Peak label	(M_1,M_2)	Frequency MHz	J′ = 61 (F_1,F_2)	J ″= 62 (F_1,F_2)	J′ = 61 (C_1,C_2)	J ″= 62 (C_1,C_2)
A	(-5/2,-1/2)	414.877	(58.5,60.5)	(59.5,61.5)	(-310,-70)	(-315,-71)
B	(5/2,-3/2)	286.741	(63.5,59.5)	(64.5,60.5)	(305,-191)	(310,-194)
C	(3/2,-1/2)	731.932	(62.5,60.5)	(63.5,61.5)	(178,-70)	(181,-71)
D	(5/2,1/2)	451.463	(63.5,61.5)	(54.5,62.5)	(305,53)	(310,54)

From this, we are able to setup 4 equations:

$$\text{Peak A} \qquad 414.877\,\text{MHz} = -190\ a' + 193\ a'' + 0.062864\ \Delta b \tag{14}$$

$$\text{Peak B} \qquad 286.741\,\text{MHz} = 57\ \Delta a + 0.210202\ \Delta b \tag{15}$$

$$\text{Peak C} \qquad 731.932\,\text{MHz} = 54\ \Delta a - 0.261929\ \Delta b \tag{16}$$

$$\text{Peak D} \qquad 451.463\,\text{MHz} = 179\ a' - 182\ a'' + 0.040367\ \Delta b \tag{17}$$

Summing (14) + (17) = (18), (16) + (15) = (19) and applying that $\Delta a = a' - a''$ we derive:

$$866.340\,\text{MHz} = -11\ \Delta a + 0.103231\ \Delta b \tag{18}$$

$$1018.67\,\text{MHz} = 111\ \Delta a - 0.051727\ \Delta b \tag{19}$$

The solution of this system is:

$$a = 13.772\,\text{MHz} \tag{20}$$

$$b = 9859.74\,\text{MHz} \tag{21}$$

This can be done using other measurements, too. To keep the effort on a realistic level, we restrict on those lines. The system gives the same equations when only lines from one group (of four peaks in the spectrum) are taken.

4.2 Evaluation of hyperfine sodium spectrum

We observe the $2S_{1/2}$–$2P_{1/2}$ transition of sodium. The peaks observed in the spectra are numbered from one to nine (figure 4).

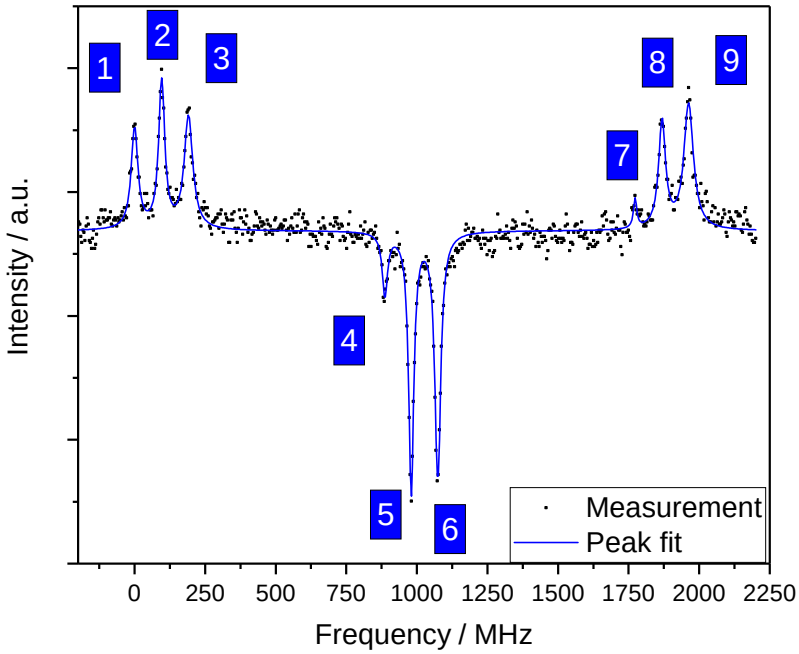


Figure 4: Measurement of Sodium at 90°C. The peaks are fitted with a Lorentz-profile (blue) and numbered from left (low frequency) to right. Nine peaks are visible in the spectrum and numbered from left to the right.

The peaks from the literature can be assigned to the transitions we observed in the spectrum (figure 5). The line in the middle between the two upper/lower states is exactly in the middle of the two states. A transition into this state occurs when the excitation energy is equal to the upper/lower state plus/minus a Doppler shift, induced by the kinetic energy of the atom. The number of the peaks in figure 4 are exactly the same like they are drawn in the energy scheme, figure 5.

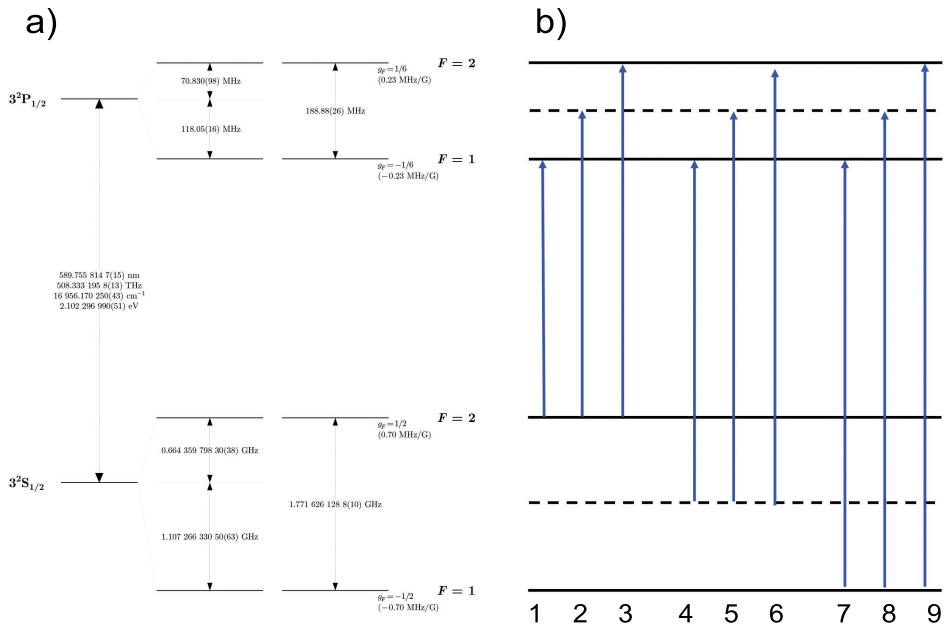


Figure 5: a) Sodium D_1 transition hyperfine structure with frequency splitting between the energy levels, taken from [5]. b) Transitions arranged in the way as they are visible in the spectrum. The middle line between the two upper/lower state is a result of the doppler shift.

Fitting the peaks in the measurement with a gaussian profile we receive the accurate position of them (table 3). With those, we are able to calculate the a value.

Table 3: Peakpositions of the Na-spectrum taken from the spectrum as well as possible transitions according to figure 5.

Peak number	Measured frequency MHz	FWHM MHz	Literature frequency MHz
1	0.0	29.033908	0.0
2	96.10	25.933931	94.5
3	191.00	36.713596	188.88
4	886.75	22.364388	885.81
5	980.10	22.026381	980.25
6	1074.12	25.453191	1074.69
7	1773.09	13.946101	1771.63
8	1868.60	29.812346	1866.50
9	1962.62	40.772949	1960.51

Applying equation 5 we can assume the a value for the transition. The nuclear Spin for Sodium is $I = 3/2$ and the F and the J quantum numbers are taken from the energy scheme and the same

for the both upper/lower states. We solve the equation for the upper $3^2P_{1/2}$ -transition:

$$\Delta E_{\text{mhfs}} = E(F=2) - E(F=1)$$
$$\Delta E_{\text{mhfs}} = \frac{a}{2}\left[2(2+1) - I(I+1) - J(J+1)\right] - \frac{a}{2}\left[1(1+1) - I(I+1) - J(J+1)\right]$$

The I and the J number are equal in both states. Therefore, we can simplify:

$$\Delta E_{\text{mhfs}} = \frac{a}{2}\left[6-2\right] = 2a$$

The result is independent of J and I as long as they are the same in both observed states. Therefore this result is also valid for the $3^2S_{1/2}$ -transition.
With the measurements in table 3 we are able to calculate the a-constant for the upper state:

$$\Delta E_{\text{mhfs}}{}^1\!/_h = \nu_{peak\ 3} - \nu_{peak\ 1} \tag{22}$$
$$\Delta E_{\text{mhfs}}{}^1\!/_h = 191.00\,\text{MHz} - 0\,\text{MHz} \tag{23}$$
$$\Longleftrightarrow a'' = 95.5\,\text{MHz} \tag{24}$$

Analog to that, the value for the lower state is calculated to

$$a' = 885.81\,\text{MHz} \tag{25}$$

5 Conclusion

As was shown in detail we studied the spectra of iodine and sodium using high resolution spectroscopy, we are interested in implementing this type of measurement since we get a Doppler free spectra, thus reducing the broadening in the absorption spectrum. Sodium demonstrated unexpected spectra as due to of four hyperfine structure levels would expect to observe four peaks in the spectra. However, the measured spectra contained nine different peaks. One can explain the unexpected peaks due to a virtual state between hyperfine states, which the transition between a virtual state state to actual hyperfine states gave rise to a peaks. With this information we could find the magnetic dipole interaction a and in the case of iodine we could find the electric dipole interaction b. The parameters were calculated in the previous section and any deviation form the expected value can be attributed to a a couple of factors, first we can consider that the formulation used is an approximation which is not the complete set of interactions given, the alignment of the setup is also very critical since we are interested in a high resolution Doppler free spectra we need both lasers to over lap to have a favorable measurement. Any other of the lasers modulation noise can also play a role in the accuracy of the spectrum.

References

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