

Hyperfine structure and isotope shift studies of rhenium by laser optogalvanic spectroscopy

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Abstract. Doppler-limited high resolution laser optogalvanic spectra of six transitions of rhenium lying in the range 560–620 nm have been recorded. Isotope shifts between the two natural isotopes of rhenium, ^{185}Re and ^{187}Re , have been calculated in all the six transitions. Hyperfine coupling constants for eight levels belonging to the configurations $5d^36s^2$, $5d^66s$, $5d^46s^26p$ and $5d^56s6p$ are reported. Wherever possible our constants are compared with those given by others.

Keywords. Hyperfine coupling constant; isotope shifts; laser optogalvanic spectra.

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1. Introduction

Rhenium is one of the transition elements with $Z = 75$. It has two stable isotopes; one with $A = 185$, nuclear spin $I = 5/2$, nuclear magnetic dipole moment $\mu_I = 3.1718 \mu_N$, electric quadrupole moment $Q_I = 2.8 \text{ b}$ and natural abundance 37.07% and other with $A = 187$, nuclear spin $I = 5/2$, nuclear magnetic dipole moment $\mu_I = 3.2043 \mu_N$, electric quadrupole moment $Q_I = 2.6 \text{ b}$ and natural abundance 62.93 (Lederer *et al* 1968). Since both the isotopes have same nuclear spin, $5/2$, and nearly the same nuclear moments, both of them show similar hyperfine spectra. The only distinguishing factor is their relative intensity, which is proportional to their natural abundance. Doppler width of rhenium spectral lines is small owing to its large atomic mass. Therefore most of the rhenium transitions are well resolved even with the Doppler-limited resolution.

In the effective operator formalism the hyperfine structure parameters are expressed as linear combinations of the radial parameters a_{nl}^{ij} and b_{nl}^{ij} (Sandars and Beck 1965). These parameters which give information about the various contributions to the hyperfine Hamiltonian, are evaluated from the experimental data. Therefore, knowledge of hyperfine structure of as many states as possible is desirable. The hyperfine structure theory and the details of calculations can be found in the review article by Lindgren and Rosen (1974). A more recent review of the theory and the hyperfine structure results in $4d$ - and $5d$ -shell elements is by Büttgenbach (1982).

Hyperfine structure measurements of 15 levels of rhenium belonging to the configurations $5d^56s^2$, $5d^56s6p$, $5d^56s7s$, $5d^66s$, $5d^66p$ and $5d^46s^26p$, were first of all studied by Hohberg *et al* (1965) using Fabry-Perot interferometer and a spectrograph. Buchholz *et al* (1979) presented some studies on isotope shift between

the two natural isotopes, 185 and 187, of rhenium and used this data for the configuration identification. Buttgenbach *et al* (1981) studied hyperfine structure of ^{185}Re and ^{187}Re in the states $5d^5 6s^2 6S_{5/2}$ and $4P_{5/2}$ using ABMR method. They also reported hyperfine structure measurements in the states $5d^5 6s^2 4G_{5/2}$ and $5d^6 6s^6 D_{9/2}$ of ^{187}Re . Bürger *et al* (1982) reported results of extensive studies performed on rhenium. They recorded high resolution spectra of 14 transitions starting from the metastable states of rhenium belonging to the configurations $(5d + 6s)^7$, by laser induced fluorescence in an atomic beam. From this spectra, they deduced isotope shifts for all the transitions and hyperfine coupling constants for 13 metastable and nine excited states. In addition, they employed ABMR method coupled with the laser induced state selective detection of metastable states to study hyperfine structure of five metastable states. Kropp *et al* (1986) used optical interferometric technique to study the isotope shift in 18 transitions and hyperfine structure of eight levels of rhenium.

Rhenium is a highly refractory element and therefore production of free atoms by thermal methods is not convenient. We employed an alternate method; sputtering in a hollow cathode discharge. This method is convenient because sputtering efficiency does not depend on the refractory nature of the element. Another advantage of this technique is that in a discharge all the metastable states emanating from the even parity configurations of the type $(6s + 5d)^7$ are populated to some extent. Therefore extensive hyperfine structure investigations can be carried out on rhenium.

In the present work high resolution optogalvanic spectra of six transitions of rhenium are reported. Isotope shift between ^{185}Re and ^{187}Re is reported for all the six transitions. Hyperfine coupling constants, A and B, for both the isotopes are reported for the levels $a^6D_{3/2, 5/2, 9/2}$, $a^4P_{5/2}$, $z^6D_{3/2, 5/2}^0$, $z^6P_{3/2, 7/2}^0$.

2. Experimental

Experimental set-up used for studying the hyperfine structure and isotope shift is similar to the one already described earlier (Singh *et al* 1990). A rhenium/neon hollow cathode discharge lamp (Instrumentation Laboratory Inc. USA) was used as a source of atoms and the detector. The lamp was usually operated at 15 mA of current. A ring dye laser (Spectra Physics 380 D) which usually gave a line width of 1 MHz and which could be tuned electronically over a range of 30 GHz, was used for excitation of the rhenium atoms present in the discharge. The maximum output power of the dye laser was 150 mW. The frequency calibration was achieved by recording the transmission peaks of a 300 MHz FSR Fabry-Perot interferometer. Chopping frequency was adjusted in the range 300 to 700 Hz, to get the minimum noise.

3. Results and discussion

High resolution optogalvanic spectra of six transitions of rhenium, lying in the range 560–620 nm, were recorded. All these transitions along with their level assignments are given in table 1. The level assignments are taken from Klinkenberg *et al* (1957). Figure 1 shows a part of the fine structure level diagram of rhenium and the transitions studied. Isotope shift between the two natural isotopes, 185 and 187, of rhenium is given in the fourth column of table 1 and in the fifth column isotope shifts reported by others are given for comparison.

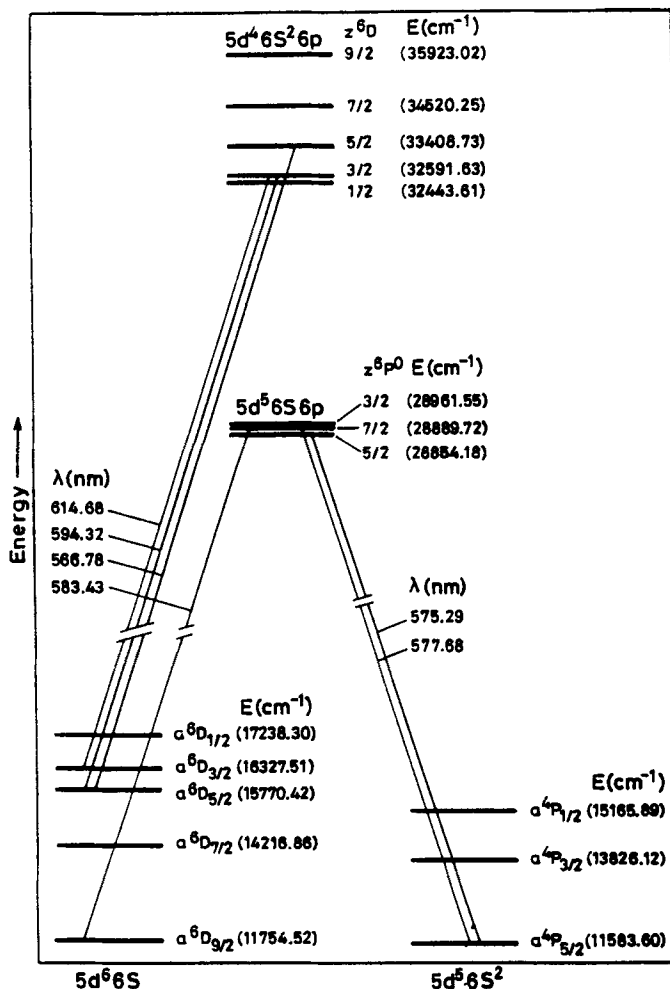


Figure 1. A part of the energy level diagram of rhenium showing the transitions studied.

Table 1. Hyperfine structure and isotope shifts of rhenium transitions studied.

Wavelength (nm)	Lower level	Upper level	Isotope shift (MHz)		
			Ours	Others	Ref.
566.78	$a^6 D_{5/2}$	$z^6 D_{5/2}^0$	307.5	—	—
575.29	$a^4 P_{5/2}$	$z^6 P_{3/2}^0$	-1481.0	-1452	^a
577.68	$a^4 P_{5/2}$	$z^6 P_{7/2}^0$	1504.0	1519	^b
583.43	$a^6 D_{9/2}$	$z^6 P_{7/2}^0$	872.1	882	^b
594.32	$a^6 D_{5/2}$	$z^6 D_{3/2}^0$	440.0	416	^b
614.68	$a^6 D_{3/2}$	$z^6 D_{3/2}^0$	1205.7	1230	^b

^aKropp *et al* 1986; ^bBurger *et al* 1982

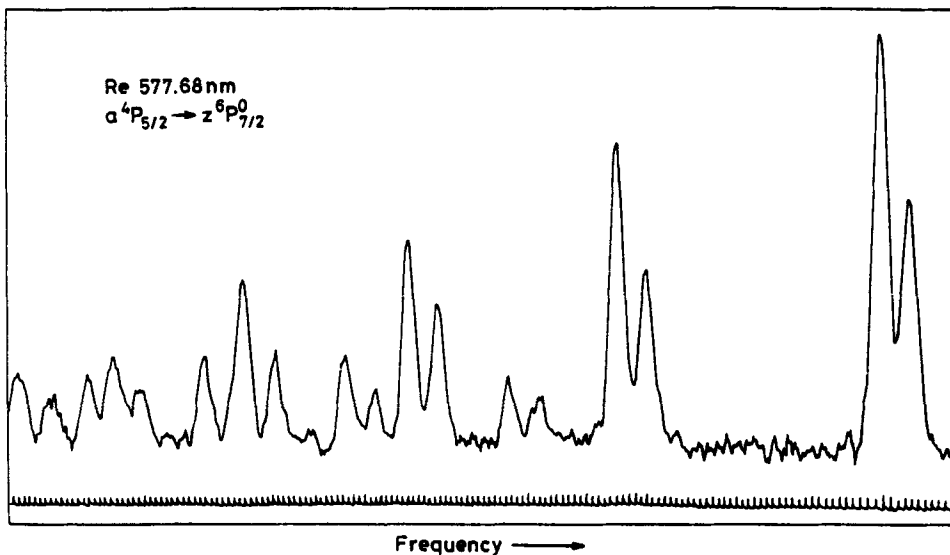


Figure 2. A typical hyperfine structure spectrum of the rhenium transition at 577.61 nm.

Figure 2 shows a typical recorded hyperfine structure spectrum of the rhenium transition at 577.61 nm. The total hyperfine structure spectrum of this transition is spread over more than 50 GHz. Therefore three overlapping spectra were recorded and joined together. The spectra were analysed using Casimir formula (Casimir 1963). Neglecting higher order terms the energy of a hyperfine level is given by

$$E_F = \frac{hAK}{2} + \frac{hB}{4} \frac{3/2K(K+1) - 2I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \quad (1)$$

where

$$K = F(F+1) - I(I+1) - J(J+1)$$

$$F = (I+J); (I+J-1); \dots |I-J|.$$

A and B are the hyperfine coupling constants for magnetic dipole and electric quadrupole interaction respectively and are given by

$$A = \frac{\mu_I H_J(0)}{hIJ} \quad \text{and} \quad B = \frac{e^2 Q_I q_J(0)}{h}$$

where $H_J(0)$ and $q_J(0)$ are the magnetic field and the electric field gradient respectively produced by the atomic electrons at the nuclear site.

Hyperfine coupling constants, A and B , of the levels involved in a particular transition were deduced from high resolution spectra of the transition. Different hyperfine components in the spectrum were identified, by comparing their relative intensities (Candler 1964; Kopfermann 1958 and Singh *et al* 1990), and used to calculate the initial values of A and B parameters. Finally spectra were analysed using a computer program based on the least square minimization procedure. In this program A 's, B 's, peak heights, half-widths of spectral line, and isotope shifts are kept as free parameters. It was necessary to keep intensities of all the peaks as free parameters because the observed relative intensities of the different hyperfine components differ

considerably from the theoretically calculated values. The deviation is mainly due to saturation of the *hfs* components (Engleman *et al* 1987). However, this saturation is not going to affect our final A's and B's because it is the peak position and not the intensity that determines these parameters. Figure 3 shows the computer fitted spectrum of the same transition.

Calculated hyperfine coupling constants, A and B, for eight levels of ^{185}Re are given in table 2; known constants are also included for comparison. Table 3 gives A and B constants for the same eight levels of ^{187}Re along with already known constants, wherever applicable. Uncertainty in A constants is of the order of 10 MHz, in B constants of the order of 40 MHz and in isotope shift it is of the order of 30 MHz. It can be seen that agreement between our values and those of others is quite good except for the B constants for the levels $a^4P_{5/2}$ and $z^6P_{3/2}^0$. This large uncertainty in B constants may be due to the large Doppler width of the spectral lines. It was also

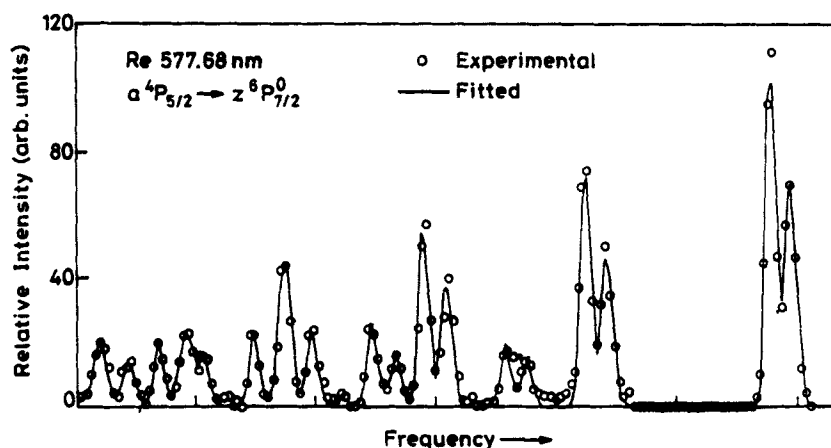


Figure 3. Computer fitted *hfs* spectrum of the rhenium transition at 577.61 nm.

Table 2. Calculated A and B constants for various levels of ^{185}Re .

Level	Our values		Others' values		Ref.
	A(MHz)	B(MHz)	A(MHz)	B(MHz)	
$5d^6 6s$					
$a^6 D_{3/2}$	1462.9	-590.4	1456.4	-561.3	b
$a^6 D_{5/2}$	1073.3	36.8	1072.2	20.1	b
$a^6 D_{9/2}$	2588.3	2415.1	2584.7	2370.4	b
$5d^5 6s^2$					
$a^4 P_{5/2}$	876.6	1738.0	880.4443	1618.529	c
$5d^4 6s^2 6p$					
$z^6 D_{3/2}^0$	23.5	960.5	18.3	954.8	b
$z^6 D_{5/2}^0$	1256.98	635.14	1262.8	636.2	b
$5d^3 6s 6p$					
$z^6 P_{3/2}^0$	3957.6	500.0	3959.4	261.0	a
$z^6 P_{7/2}^0$	2855.4	1145.9	2819.7	1051.8	b

^aKropp *et al* 1986; ^bBurger *et al* 1982; ^cButtgenbach *et al* 1981

Table 3. Calculated A and B parameters for various levels of ^{187}Re .

Level	Our values		Others' values		Ref.
	A(MHz)	B(MHz)	A(MHz)	B(MHz)	
$5d^6 6s$					
$a^6 D_{3/2}$	1493.8	-510.8	1470.3	-531.1	^b
$a^6 D_{5/2}$	1091.7	15.6	1083.6	21.6	^b
$a^6 D_{9/2}$	2637.2	2231.2	2611.2	2251.7	^b
$5d^5 6s^2$					
$a^4 P_{5/2}$	896.5	1750.0	889.2413	1531.466	^c
$5d^4 6s^2 6p$					
$z^6 D_{3/2}^0$	28.8	985.5	18.8	905.1	^b
$z^6 D_{5/2}^0$	1283.4	579.9	1275.1	600.7	^b
$5d^5 6s 6p$					
$z^6 P_{3/2}^0$	4027.8	500.0	—	—	
$z^6 P_{7/2}^0$	2885.4	915.0	2848.2	1001.9	^b

^bBurger *et al* 1982; ^cButtgenbach *et al* 1981

observed that the average line-width of these spectral lines is 1000 MHz, which corresponds to an equilibrium atomic temperature 1100 K.

In conclusion, isotope shifts between ^{185}Re and ^{187}Re , in six transitions are reported. Hyperfine coupling constants, A and B, for eight levels; $5d^6 6s a^6 D_{3/2, 5/2, 9/2}$, $5d^5 6s^2 a^4 P_{5/2}$, $5d^4 6s^2 6p z^6 D_{3/2, 5/2}^0$, and $5d^5 6s 6p z^6 P_{3/2, 7/2}^0$ of both the isotopes are reported. It is hoped that the data presented here will be useful for further theoretical analysis which will help in understanding this complex atom.

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