Experimentally determined oscillator strengths in Rh II

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Abstract

This paper presents new experimentally determined branching fractions and oscillator strengths (log \(g_f\)) for lines originating from 17 levels belonging to 5 terms of the first excited odd configuration \(4d^7(4D)5p\) in Rh II. The intensity calibrated spectra of Rh II have been recorded with a Fourier transform spectrometer between 25000 and 45000 cm\(^{-1}\) (2200–4000 Å). In this region, 49 lines have been identified and measured. By combining the branching fractions obtained from the spectra with previously measured lifetimes, log \(g_f\) values are reported. The new results are compared with previous theoretical work. (Some figures may appear in colour only in the online journal)

1. Introduction

Rhodium is one of the most expensive metals on earth and finds its use in the automotive industry as a catalyst. Of more scientific interest is the fact that rhodium has been detected in the spectra of many astrophysical objects e.g. the sun [1], and the HgMn-type stars \(\chi\) Lupi [2], HD 65949 [3] and HD 175640 [4]. The need for accurate and reliable atomic data in order to investigate high-resolution spectra from objects such as these is significant, and to the best of our knowledge no experimental oscillator strengths are available for Rh II. In a recently published study, Quinet et al [5] combined measured lifetimes with theoretical branching fractions (BFs) and derived semi-empirical oscillator strengths. The lifetime measurements were performed on ions in a laser-generated plasma employing the time-resolved laser-induced-fluorescence technique, and the calculations were performed with a relativistic Hartree–Fock model with core-polarization (HFR+CPOL). This paper aims to experimentally evaluate the reliability of these oscillator strengths and further enhance our knowledge of Rh II.

A schematic drawing of the lower part of the energy level structure of singly charged rhodium can be seen in figure 1. When measuring BFs, extensive knowledge of the energy level structure of the system of interest is necessary since accurate values require the measurements of all lines originating from an upper level. The line list used in this work was compiled by Kramida et al [6] and based on earlier work by Sancho [7]. In this study, BFs for transitions from terms belonging to the first excited \(d^7(4D)5p\) configuration are measured and combined with previously published experimental lifetimes [5]. More specifically, levels belonging to the terms \(z^5F^0\), \(z^5D^0\), \(z^5G^0\), \(z^5F^0\) and \(z^5G^0\) are investigated.

The main decay channel for the quintet terms in the \(4d^7(4D)5p\) configuration is to levels in the \(a^3F\) term belonging to the configuration \(4d^8(4F)5s\). However, they also decay by inter-combination transitions to states in the ground configuration \((4d^8\ a^3F)\). The latter transitions fall in the vacuum UV, and cannot be measured in the present experiment. This is a potential problem in the BF determinations for these levels. However, in most cases, the inter-combination lines...
are weak and their influence can be estimated from these theoretical calculations.

2. Experiment

To determine the oscillator strengths, it is necessary to measure the lifetime of the upper level as well as the relative intensities of all lines originating from that level. The branching fraction, BF, is defined as

\[ BF_{ul} = \frac{A_{ul}}{\sum_k A_{uk}} = \frac{I_{ul}}{\sum_k I_{uk}}, \]

where \( u \) labels the upper and \( l \) the lower level, respectively. \( A \) is the transition probability and \( I \) is the measured intensity in units of number of photons per second on an accurately calibrated scale over the whole wavelength range. Combining the BFs with the lifetime defined as

\[ \tau_u = \frac{1}{\sum_k A_{uk}}, \]

allows for the extraction of the individual \( A_{ul} \)-values as

\[ A_{ul} = BF_{ul} / \tau_u. \]

The oscillator strength, \( f_{ul} \), is then derived through the formula

\[ f_{ul} = 1.499 \times 10^{-16} \times \frac{\sigma_{ul} \lambda_{ul}^2}{g_l}, \]

where \( g \) is the statistical weight and \( \lambda_{ul} \) is the wavelength (in Å) of the transition in question.

Figure 1. An energy level diagram of singly ionized rhodium. The solid arrows show transitions that can be readily measured with our experimental setup. The dashed line indicates transitions down to the ground configuration which, in some cases, fall outside the range of our setup.

Figure 2. Two spectra recorded with different detectors, Hamamatsu 1P28 (below) and Hamamatsu R166 (above). The intensity scales are shifted vertically for the purpose of illustration. Lines in the overlapping region are used to relate the different intensity scales.

2.1. Determination of branching fractions

A hollow cathode (HC) discharge was used as the emission light source. The HC has a hollow iron core where a thin foil, 0.125 mm thick and 25 × 25 mm wide, was inserted. The foil consisted of 99.9% rhodium. The HC was operated at currents between 0.1 and 1 A and neon was used as a carrier gas. The typical pressures during the measurements were around 1.6–1.8 torr. The light emitted from the cathode was analysed by an FTS instrument (Chelsea Instruments FT500).

The instrument itself restricts the wavelength region to be covered in the spectra since it has a beamsplitter which cuts off at 1850 Å. However, this was not the main limitation since the optical path between the HC and the FTS instrument was in air, hence no wavelengths below 2000 Å could be measured. Another restriction posed on the obtained spectra is the sensitivity of the detectors used when recording the spectra. To cover the region of interest, two different detectors were used. In the region between 25000 and 40000 cm\(^{-1}\), a Hamamatsu 1P28 photo multiplier tube (PMT) was used, whereas the region between 35000 and 45000 cm\(^{-1}\) was covered by a Hamamatsu R166 PMT. To avoid the aliasing inherent in the FTS method, a standard UG5 coloured glass filter (cutoff around 6500 Å) was used in combination with the 1P28 detector to limit the aliasing with longer wavelengths where the detector is sensitive. In figure 2, two complete spectra recorded with the two different detector setups are shown, displaying their sensitivity, as well as their relative strengths in the overlapping region.

Promptly after measuring a series of rhodium spectra, a spectrum of a calibrated deuterium lamp was recorded. The deuterium spectrum was then used to determine the response of the detectors. For the determination of BFs, no absolute calibration is necessary; only the relative intensities are of interest. However, the spectra recorded with the different detectors have to be brought to a common scale. This was done by comparing the intensities of lines recorded by both detectors in the overlapping region. Thus, the scaling factor between the two regions was determined by taking the ratios
Table 1. Experimental oscillator strengths, log $gf$ values and branching fractions together with theoretical.

| Upper level | $\tau^+$ (ns) | Lower level | $\lambda^b$ (nm) | BF | $\log(gf)$ |
|-------------|---------------|-------------|-----------------|----|------------|
| $^3$G$_6^+$ | 3.0(2)        | $^3$G$_6^+$ | 233.477         | 1  | 0.549      |
| $^3$P$_1$   | 3.9(5)        | $^3$F$_5$   | 252.052         | 0.874 | 12.8      |
|             |               | $^3$F$_4$   | 263.033         | 0.068 | 14.7      |
|             |               | $^3$G$_4$   | 320.725         | 0.022 | 14.5      |
|             |               | $^3$P$_3$   | 347.776*        | 0.019 | 14.5      |
|             |               | Residual    | 0.017           |     |            |
| $^3$F$_5$   | 3.8(3)        | $^3$F$_5$   | 249.079         | 0.957 | 7.9       |
|             |               | $^3$P$_3$   | 315.929         | 0.038 | 10.6      |
|             |               | Residual    | 0.004           |     |            |
| $^3$F$_1$   | 3.8(3)        | $^3$F$_4$   | 251.065         | 0.875 | 8.0       |
|             |               | $^3$F$_3$   | 259.216         | 0.076 | 12.4      |
|             |               | $^3$G$_4$   | 323.332         | 0.020 | 11.2      |
|             |               | $^3$P$_2$   | 330.734*        | 0.017 | 11.1      |
|             |               | residual    | 0.009           |     |            |
| $^3$D$_3^+$ | 3.2(2)        | $^3$F$_5$   | 236.467         | 0.051 | 9.3       |
|             |               | $^3$F$_4$   | 246.103         | 0.912 | 6.1       |
|             |               | $^3$P$_3$   | 318.783         | 0.033 | 9.4       |
|             |               | Residual    | 0.004           |     |            |
| $^3$F$_2$   | 3.8(3)        | $^3$F$_3$   | 250.512         | 0.826 | 8.0       |
|             |               | $^3$F$_2$   | 255.992         | 0.120 | 12.0      |
|             |               | Residual    | 0.038           |     |            |
| $^3$G$_4^+$ | 3.5(2)        | $^3$F$_5$   | 233.330         | 0.066 | 19.2      |
|             |               | $^3$F$_3$   | 242.709         | 0.568 | 6.4       |
|             |               | $^3$G$_4$   | 291.015         | 0.313 | 7.8       |
|             |               | residual    | 0.053           |     |            |
| $^3$D$_3^+$ | 3.4(4)        | $^3$F$_4$   | 238.545         | 0.047 | 14.0      |
|             |               | $^3$F$_3$   | 245.890         | 0.891 | 11.8      |
|             |               | $^3$P$_2$   | 309.344         | 0.028 | 14.7      |
|             |               | Residual    | 0.034           |     |            |
| $^3$G$_4$   | 3.3(3)        | $^3$F$_3$   | 241.584         | 0.708 | 8.2       |
|             |               | $^3$F$_2$   | 279.278         | 0.036 | 21.3      |
|             |               | $^3$P$_2$   | 296.354         | 0.115 | 10.5      |
|             |               | residual    | 0.140           |     |            |
| $^3$D$_2$   | 3.7(5)        | $^3$F$_3$   | 240.522         | 0.088 | 15.2      |
|             |               | $^3$F$_2$   | 245.571         | 0.809 | 13.6      |
|             |               | $^3$P$_2$   | 300.898         | 0.049 | 16.1      |
|             |               | $^3$P$_1$   | 309.675         | 0.021 | 17.8      |
|             |               | Residual    | 0.031           |     |            |
| $^3$G$_3$   | 3.3(2)        | $^3$F$_2$   | 242.100         | 0.832 | 6.3       |
|             |               | $^3$F$_3$   | 289.763         | 0.019 | 30.4      |
|             |               | $^3$F$_2$   | 301.978         | 0.057 | 11.8      |
|             |               | residual    | 0.093           |     |            |
| $^3$G$_4$   | 3.2(2)        | $^3$F$_4$   | 229.004         | 0.587 | 6.9       |
|             |               | $^3$G$_3$   | 271.527         | 0.352 | 7.6       |
|             |               | residual    | 0.062           |     |            |
| $^3$F$_2$   | 3.3(3)        | $^3$F$_1$   | 243.185         | 0.875 | 9.1       |
|             |               | $^3$F$_2$   | 298.830         | 0.049 | 21.1      |
|             |               | residual    | 0.076           |     |            |
| $^3$G$_4$   | 3.4(2)        | $^3$F$_3$   | 226.343         | 0.313 | 7.4       |
|             |               | $^3$F$_3$   | 273.740         | 0.464 | 6.7       |
|             |               | $^3$P$_3$   | 276.483         | 0.087 | 9.3       |
|             |               | residual    | 0.136           |     |            |
| $^3$F$_1$   | 2.4(2)        | $^3$F$_3$   | 235.035         | 0.045 | 9.2       |
|             |               | $^3$P$_3$   | 270.560         | 0.477 | 6.5       |
|             |               | residual    | 0.478           |     |            |
| $^3$F$_1$   | 2.3(3)        | $^3$F$_2$   | 233.530         | 0.042 | 19.4      |
|             |               | $^3$F$_1$   | 262.541         | 0.360 | 13.5      |
|             |               | $^3$P$_3$   | 277.577         | 0.098 | 16.4      |

*Residual values and branching fractions together with theoretical.
Table 1. (Continued.)

| Upper level | $\tau$ (ns) | Lower level | $\lambda$ (nm) | BF | log $gf$ |
|--------------|-------------|-------------|----------------|----|---------|
| $z^3G_o^3$  | 2.0(3)      | $a^5F_4$    | 223.771        | 0.099 | 0.095 | 8.8 | $-0.602$ | 17.4 |
| $b^5F_4$    | 250.276     | $b^3F_3$    | 263.900        | 0.078 | 0.076 | 6.4 | $-0.554$ | 16.1 |
| $a^5F_3$    | 266.448     | $a^5F_2$    | 273.992        | 0.022 | 0.021 | 17.9 | $-1.11$  | 23.4 |
| $b^3F_2$    | 273.992     | Residual    | 0.483          | -     | -      | -   | $-0.022$ | 15.6 |

$^a$ Lifetimes and theoretical BFs from Quinet et al [5].

$^b$ The wavelengths are from Sancho [7] except the starred ones which are calculated from the energy levels.

Figure 3. The observed line corresponding to the $b^3F_4-z^5F_o^5$ transition around 31 643.9 cm$^{-1}$ together with a fitted Gaussian line shape function.

Figure 4. Ratio between our measured branching fractions, BF$_{exp}$, and the theoretical branching fractions from [5], BF$_{theory}$, plotted against BF$_{exp}$.

3. Results

Rhodium has only one stable isotope which makes the interpretation of the spectra easier with no isotope shift present. Furthermore, it has a nuclear spin of $I = 1/2$ so at most two possible hyperfine components of each level are possible. However, this splitting was too small to be resolved. For all the observed lines, the GFit [8] software was used to fit Gaussian line shapes to determine line positions as well as to obtain the area of the peaks.

The fits were in general good and the result of one particular fit can be seen in figure 3. The line in the figure has a full-width at half-maximum of 0.155(2) cm$^{-1}$ at 31643.9 cm$^{-1}$. For some of the strongest lines (with $A$-values around $10^9$ s$^{-1}$), a small asymmetry was observed which affected the goodness-of-fit, but to a lesser extent the uncertainty in the area determination. The reason for this asymmetry is most likely imperfections in the alignment of the optical path of the FTS instrument. In the determination of the oscillator strengths, there are several uncertainties contributing to the final uncertainty stated in table 1: the uncertainty in the area determination, the intensity calibration of the spectra (with the use of the deuterium lamp) and the lifetime. These are then added quadratically to obtain the total uncertainty. A detailed description of the uncertainty analysis can be found in [9]. In general, the main contributor to the uncertainty budget is the previously measured lifetimes, which in some cases have uncertainties around 15%.

Whether a line is observed or not is due to the combination of the sensitivity of the detection setup at the wavelength of the line and the intrinsic line strength. In general, lines weaker than $A \approx 4 \times 10^7$ s$^{-1}$ [5] were not observed or the signal-to-noise ratio was too low to provide a satisfactory fit of the observed line. Contributions from lines not measurable in the spectra or outside of the range of the detectors are summed up using the theoretical BF from Quinet et al [5] into a residual. The experimental BFs are then adjusted to accommodate the missing branches, i.e. they are scaled down to make the sum of all measured- and estimated-residual branches equal to 1. The main decay channel for some of the triplet terms is to the ground configuration. The estimation of the missing branches for these levels can therefore be up to around 50%.

A detailed description of the uncertainty analysis can be found in [9]. In general, the main contributor to the uncertainty budget is the previously measured lifetimes, which in some cases have uncertainties around 15%.
agreement between the theoretical and experimental BFs is in general good. The ratio between the experimental and theoretical BFs plotted against the experimental BFs can be generally good. The ratio between the experimental and theoretical BFs is mostly within the uncertainty limits. However, our data suggest a slight overestimation of the deviations between our measured and the theoretical BFs are mostly within the uncertainty limits. However, our data suggest a slight overestimation of the mixing of levels in the calculations could be overestimated, resulting in stronger spin-forbidden lines. The trends in figure 5 where the spin-forbidden lines, with in general lower wavenumbers due to the energy level structure, can be seen to the left in the picture and the allowed to the right, indicating as in figure 4, that the mixing is overestimated in the calculation.

4. Conclusions

Branching fractions for 49 Rh II lines were measured for the first time using an FTS instrument and an emission source. The BFs have been combined with previously measured lifetimes by Quinet et al [5], to yield oscillator strengths for these transitions. The deviations between our measured and the theoretical BFs are mostly within the uncertainty limits. However, our data suggest a slight overestimation of the mixing leading to higher theoretical BFs—and thus \( \log(\text{gf}) \)—for the spin-forbidden lines.

Acknowledgments

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Table 2. A findings list with experimental \( \log(\text{gf}) \) ordered by increasing wavelength.

| \( \lambda \) (nm) | \( \log(\text{gf}) \) | Uncertainty |
|-----------------|----------------|-------------|
| 223.771         | -0.602         | 17.4%       |
| 226.343         | -0.214         | 7.4%        |
| 229.004         | 0.193          | 6.9%        |
| 233.330         | -0.719         | 19.1%       |
| 233.477         | 0.549          | 12.8%       |
| 233.530         | -1.13          | 19.4%       |
| 235.035         | -0.817         | 9.2%        |
| 236.467         | -0.801         | 9.2%        |
| 238.545         | -0.989         | 14.1%       |
| 240.522         | -0.977         | 15.2%       |
| 241.584         | -0.25          | 8.3%        |
| 242.100         | 0.204          | 6.3%        |
| 242.709         | 0.239          | 6.4%        |
| 243.185         | 0.0811         | 9.1%        |
| 245.571         | -2.62 \times 10^{-3} | 13.6% |
| 245.890         | 0.217          | 11.8%       |
| 246.103         | 0.348          | 6.1%        |
| 249.079         | 0.416          | 7.9%        |
| 250.276         | 0.566          | 16.1%       |
| 250.512         | 0.00724        | 8.0%        |
| 251.065         | 0.183          | 8.0%        |
| 252.052         | 0.284          | 12.8%       |
| 255.992         | -0.789         | 12.0%       |
| 259.216         | -0.792         | 12.4%       |
| 262.541         | 0.0933         | 13.5%       |
| 263.033         | -0.73          | 14.7%       |
| 263.900         | -0.554         | 16.3%       |
| 266.448         | -1.11          | 23.4%       |
| 270.560         | 0.289          | 6.5%        |
| 271.527         | 0.137          | 7.6%        |
| 273.740         | 0.151          | 6.7%        |
| 273.992         | -0.0217        | 15.6%       |
| 276.483         | -0.575         | 9.3%        |
| 277.577         | -0.577         | 16.4%       |
| 279.278         | -1.06          | 21.3%       |
| 289.763         | -1.36          | 30.4%       |
| 291.015         | -0.00584       | 7.8%        |
| 296.354         | -0.509         | 10.5%       |
| 298.830         | -1.27          | 21.1%       |
| 300.898         | -1.13          | 16.1%       |
| 301.978         | -1.02          | 11.8%       |
| 309.344         | -1.14          | 14.7%       |
| 309.675         | -1.41          | 17.8%       |
| 315.926         | -0.932         | 10.6%       |
| 318.783         | -0.972         | 9.4%        |
| 320.725         | -1.22          | 14.5%       |
| 323.332         | -1.36          | 11.2%       |
| 330.734         | -1.39          | 11.1%       |
| 347.776         | -1.24          | 14.5%       |

a The wavelengths are from Sancho except the starred which are calculated from the energy levels.

Figure 5. Ratio between our measured branching fractions, \( \text{BF}_{\text{exp}} \), and the theoretical branching fractions from Quinet et al [5], \( \text{BF}_{\text{theory}} \), plotted against wavenumber.
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