Isotope shifts for the $5d^56s\,7s$ and $5d^56s\,6d$ configurations of Re I

H.-D. Kronfeldt $^1$, D. Ashkenasi $^1$, G. Basar $^{1,*}$, L. Neale $^2$, M. Wilson $^2$

$^1$ Optisches Institut, Technische Universität Berlin, Strasse des 17. Juni 135, W-1000 Berlin 12, Federal Republic of Germany
$^2$ Department of Physics, Royal Holloway and Bedford New College, University of London, Egham, Surrey TW20 0EX, UK

Received: 2 October 1992

Abstract. The isotope shift and hyperfine structure in a rhenium hollow cathode discharge was studied for transitions of the type $5d^56s\,7s\rightarrow5d^56s\,6p$ and $5d^56s\,6d\rightarrow5d^56s\,6p$ through Doppler-free saturation absorption laserspectroscopy and high resolution interferometry. Taking configuration mixing in the lower levels of $5d^56s\,6p$ under consideration, we obtain average configuration isotope shift values for $5d^56s\,7s$ of $-1760(100)$ MHz and for $5d^56s\,6d$ of $-1930(200)$ MHz. These experimental values compare extremely well with the theoretically predicted configuration isotope shifts in rhenium, based on pseudo-relativistic Hartree-Fock calculations, of $-1710$ MHz and $-1940$ MHz, resp. In addition hyperfine structure constants for rhenium levels of $5d^56s\,6d$ are reported here for the first time.

PACS: 32.30.Jc; 35.10.Bg

1. Introduction

Precise information on the isotope shift (IS) and hyperfine structure (hfs), derived from high resolution spectroscopical methods, provides a sensitive test of theoretical models used to describe internal atomic interactions such as configuration interactions and relativistic fine structure (fs) effects. For this reason much effort has been spent in recent years to obtain systematic studies of hfs and IS especially for the heavier elements – see compilations [1, 2].

Some of the $5d$-elements such as Re are highly refractory thus making laserrspectroscopic measurements in their vapour a challenging task. However, a few highly sophisticated studies probing the hfs and IS of Re I have already been accomplished. In 1981 Büttenbach et al. [3] performed precise measurements of optical transitions of metastable low-lying Re levels and contributed a fs calculation of the even configurations $(5d+6s)^6p$, taking into account the electrostatically correlated spin-orbit interaction in second order for the interpretation of their experimental hfs- and IS data. For the odd configurations $(5d+6s)^6p$ the fs-calculations of Wyart [4] show that the configuration interaction between $5d^56p$, $5d^26s6p$, and $5d^46s^26p$ is extremely strong. Also the very large spin-orbit interactions within each configuration leads to strong mixing of levels based on different LS basis states.

One of us [H.-D.K.] has already studied level classifications in the configuration $5d^56s^26p$ in [5] and the IS and hfs of levels belonging to $(5d+6s)^6p$ configurations in [6]. Values of field shifts ($\Delta T$) for each configuration were deduced from the experimental data by the use of the sharing rule. Finally in [7] one of us [M.W.] reported pseudo-relativistic Hartree-Fock (HFR) calculations for a selection of Re I configurations. The theoretical values for the electron density at the nucleus, $4\pi|\psi(0)|^2$, proportional to the field shift, agreed quite well with the experimentally derived values in [6]. This motivated further experimental and theoretical investigations in Re. Therefore in this work the hfs and IS of the energetic high-lying Re I configurations $5d^56s\,7s$ and $5d^56s\,6d$ were investigated for which no adequate hfs and IS data exist, i.e. only the hfs for $5d^56s\,7s$ was investigated in some former works of our group [8, 9]. The experimental IS data is then compared with additional HFR calculations.

2. Procedures

2.1. Experimental

The experimental arrangement for sub-Doppler saturation absorption spectroscopy (SAS) in a see-through hollow-cathode discharge can be seen in Fig. 1. The output beam of a narrowband tunable light source (Coherent 699-29, autoscan) is split into two beams, one weak “probe” beam and an intensity modulated stronger “pump” beam. The two counter-propagating light beams overlap in the hollow-cathode discharge. The nonlinear
change in the absorption of the “probe” beam is detected by a lock-in technique. The arrangement concerning the laser system is basically the same as described in [10, 11].

To perform sub-Doppler SAS in a Re vapour a self-developed water-cooled high-current see-through hollow cathode was used in a Xe + Ar (+ Kr) discharge atmosphere with a pressure around 1.5 Torr and a discharge current of over 500 mA. While the high-current discharge enhances sputtering and excitation processes, especially important for highly refractory elements, it also reduces velocity changing collisional effects, discussed e.g. in [12, 13]. We employed the sub-Doppler method of SAS, since reliable optogalvanic detection at discharge current around ~0.5 A is a most difficult task.

In the blue-region we employed optical interferometry, as already described in [6], using a pressure scanning Fabry-Perot interferometer and a liquid nitrogen cooled hollow-cathode lamp filled with a Re foil, i.e. Re in its natural composition: 37.07% 185Re and 62.93% 187Re, just as in the SAS experiments.

2.2. Theoretical calculations

The method of calculation used to obtain the results in this work were based on the so-called pseudo-relativistic Hartree-Fock (HFR) procedure whose usefulness for isotope shift studies was first established long ago [14].

Briefly this procedure includes the mass-velocity and Darwin terms of the Pauli approximation into the usual non-relativistic Hartree-Fock (HF) Hamiltonian. This has the effect to reproducing the main effects of relativity in that the charge density distributions are much closer to those obtained from Dirac-Fock calculations than those from non-relativistic HF calculations. In addition the HFR model has the appealing feature that it ensures that calculations of level structures, isotope shifts etc., stay within the non-relativistic algebraic framework. In the present case of Re some difficulties were encountered in obtaining stable solutions for some of the wavefunctions of the new configurations studied and more than usual care had to be exercised in obtaining initial estimates and in modifying iteration controls and acceleration factors in order to coax convergence. Although term specific HFR solutions may be obtained using this procedure because of the preliminary nature of this study we confined our attentions in this work to obtaining average of configuration solutions.

3. Results and discussion

The transitions selected for IS investigations were those between levels of the configurations 5d^26s7s and 5d^26s6d to 5d^26s6p. In Table 1 the line isotope shifts AT_{line} and the experimental magnetic dipole and electric quadrupole hfs constants A and B for each transition are presented. The red Re I lines were measured with sub-Doppler SAS – a typical example of a SAS profile together with the smoothed computer fit is presented for the transition λ = 632.19 nm in Fig. 2. In this transition the large hfs splitting is dominant. The expected small IS could be determined to be AT_{line} = 30.2(3.3) MHz in this case, although the FWHM for the lorentzian profile is around 100 MHz.

The results for the hfs constants A and B of the levels investigated are compiled for the isotope 185Re in Table 2. Since the hfs-anomaly is small, 185A187 < 0.03% [16], the ratios for the constants A and B were fixed in the computer fits to A(185Re)/A(187Re) = 0.9902 and B(185Re)/B(187Re) = 1.0567 [17]. The comparison between our new hfs values with those of Bürger et al. [17] and values from our previous studies [6, 8, 9] demonstrate in most cases a good consistancy.

To discuss the IS a little further we have used the frequency-independent residual IS values for each transition AT_{res}, i.e. the easily calculable normal mass shift has been subtracted from the experimental IS-values AT_{line}. This allows us next to derive representative values of IS for the two new configurations studied. To determine the level IS in 5d^26s7s and in 5d^26s6d we must take into account possible configuration mixing in the lower levels using the ‘sharing rule’:

\[ \Delta T_{\text{lower level}} = \sum_i x_i \Delta T_i(\text{configuration}). \]