

## LETTER TO THE EDITOR

## Precision VUV spectroscopy of Ar I at 105 nm

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**Abstract.** The results of a precision measurement of the  $3p^6-3p^54s'[\frac{1}{2}]_1$  ( $1s_2$  in Paschen notation) transition in argon by resonance-enhanced 1 VUV + 1 UV photo-ionization spectroscopy at 105 nm are presented. Tunable narrow-band VUV radiation is generated by frequency up-conversion of the powerful output of a pulsed dye amplifier system. A transition frequency of  $95\,399.833(3)\text{ cm}^{-1}$  in  $^{40}\text{Ar}$  is measured, in agreement with (but an order of magnitude more accurate than) the existing value for this transition. Transition isotope shifts  $\delta\nu_{40-38} = 550(10)\text{ MHz}$  and  $\delta\nu_{40-36} = 1036(7)\text{ MHz}$  are obtained, from which specific mass shifts are deduced. An improved value for the ionization potential in argon ( $\text{IP} = 127\,109.842(4)\text{ cm}^{-1}$ ) is also given.

Over the past decade, with the development of powerful dye amplifiers and harmonic-generation techniques, the vacuum ultraviolet (VUV) spectral region became accessible with narrow-band tunable laser sources, thus making possible spectroscopic studies of transitions involving ground states of noble gas atoms with unsurpassed accuracy. The energy level structure of the noble gases is such that the entire manifold of electronically excited states is separated from the electronic ground state by a large energy gap. A laser at 58 nm was used [1] to bridge this gap in helium, resulting in accurate values for the ionization potential (IP), the ground state Lamb shift and the  $^3\text{He}-^4\text{He}$  isotope shift. Similar studies of heavier rare gases such as Ne and Kr in the VUV [2, 3] gave valuable information on the level structure of these more complex systems and at present an accuracy of  $0.005\text{ cm}^{-1}$  has been reached for some VUV transitions. However, in Ar accurate values for the VUV transition frequencies are missing; hence the ionization potential is not known accurately for this atom. Recently [4], a multichannel quantum defect analysis of the Rydberg series of  $^{40}\text{Ar}$  was reported, determining accurate values ( $\pm 0.003\text{ cm}^{-1}$ ) for the two ionization potentials ( $j_c = \frac{1}{2}, \frac{3}{2}$ ) with respect to the metastable  $^3P_2$  level ( $1s_5$  in Paschen notation), populated in a discharge.

In this letter we report on a precise calibration of the  $3p^6(^1S_0)-3p^54s'[\frac{1}{2}]_1$  ( $1s_2$ ) transition in argon by 1VUV+1UV photo-ionization using a narrow-band laser source at 105 nm. The accuracy of  $0.003\text{ cm}^{-1}$  is a factor of 15 better than the best known value of  $0.05\text{ cm}^{-1}$  [5] dating from the early 1970s. Furthermore, an analysis of the isotope shifts in the  $^1S_0-1s_2$  transition for the three stable argon isotopes (36, 38, 40) is made. In general, these shifts are due to differences in the nuclear mass (mass shifts) and nuclear charge distribution (field shifts). To a good approximation [6] the isotope shift can be presented as a sum of the mass and field shift. The latter is negligible for light elements such as argon, but it can dominate the isotope shift in heavy elements. The mass shift can be described as consisting of two parts:

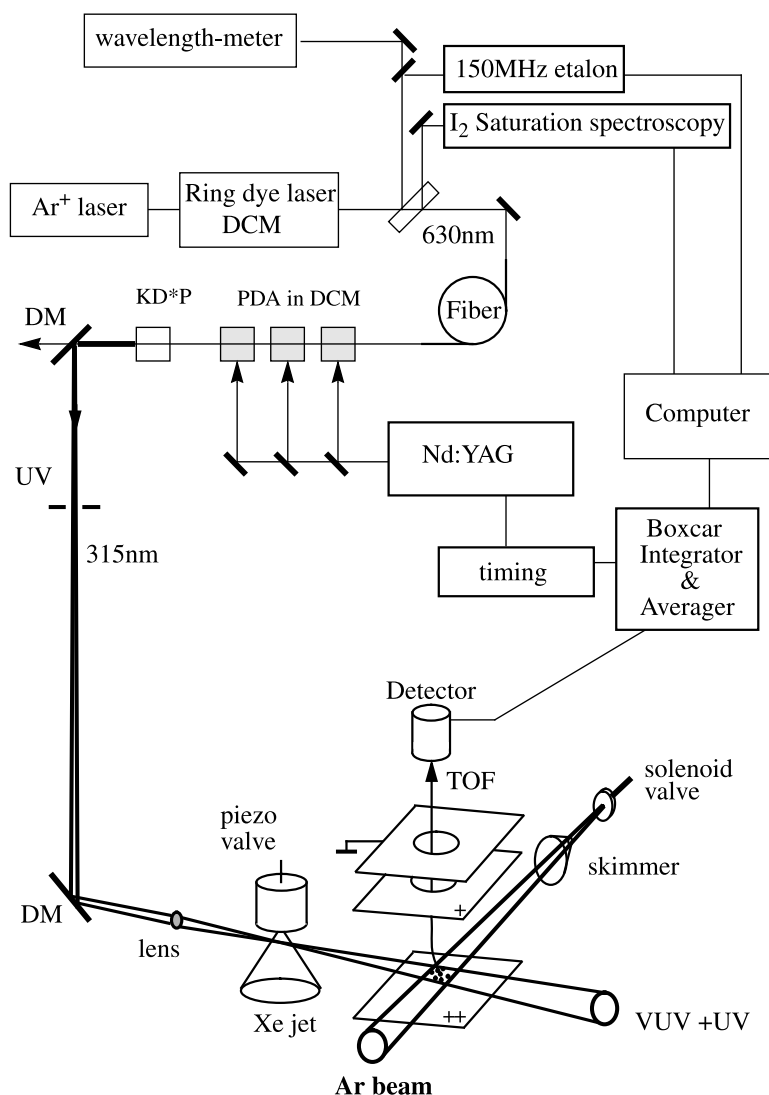
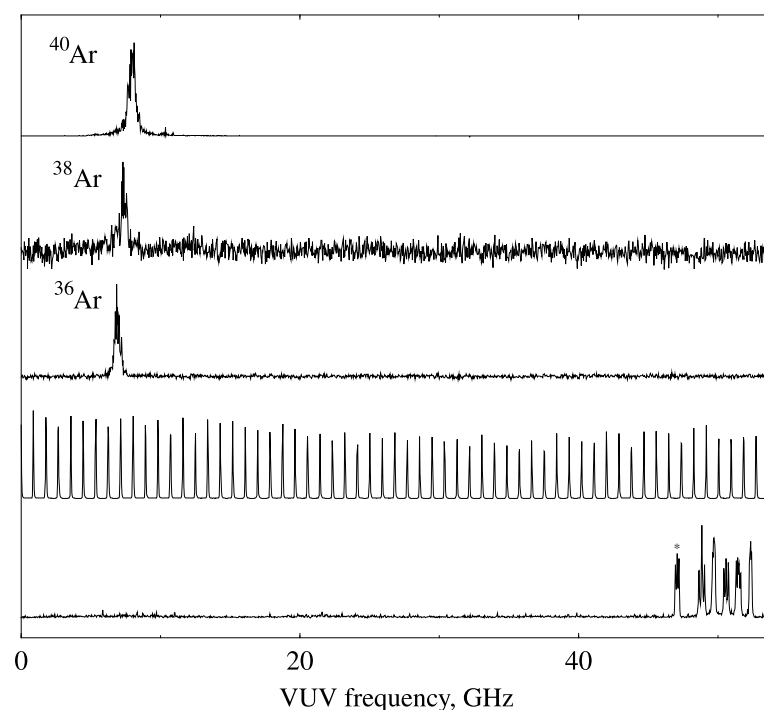


Figure 1. Experimental set-up.

the normal mass shift (NMS), also called the Bohr shift, due to the change of the reduced mass  $\mu$ , and the specific mass shift (SMS), resulting from the correlation between the momenta of all electrons in the atom. While the NMS is easy to calculate, difficult many-body calculations are needed in order to estimate the SMS [7]. In the following we give experimental values for the SMS in the  $^1S_0-1s_2$  transition for the three stable argon isotopes.

In figure 1 a schematic of the experimental set-up is presented. Tunable visible wavelengths at 630 nm are generated with an Ar-ion laser pumped continuous-wave (CW) ring dye laser operating on DCM dye and delivering 400 mW of single-mode narrow-band radiation. A sealed and temperature-stabilized etalon, which is actively locked to a frequency-stabilized HeNe laser, provides accurate frequency markers. Its free spectral range of 148.9565(4) MHz was calibrated by measuring the frequency separation between two accurately known hyperfine



**Figure 2.** A scan of the  $^1S_0-1S_2$  resonance for the three isotopes, the etalon markers and the iodine saturation spectrum of R67(9–4). The asterisk (\*) denotes the ‘t’ hyperfine component calibrated previously and used as a frequency standard at 105 nm.

components of P61(7–3) and R96(9–4) lines in molecular iodine [8]. Absolute calibration in the visible is based on the ‘t’ hyperfine component of R67(9–4) in the saturation spectrum of iodine measured for the purpose of this experiment<sup>†</sup>.

The output of the dye laser is coupled into a polarization-maintaining single-mode fibre (3M, FS-PM-3-21) for beam transportation to the pulsed part of the experiment as well as for spatial filtering. The fibre output (200 mW) seeds a three-stage pulsed dye amplifier (PDA) also operating on the DCM dye, which is pumped by a frequency-doubled (532 nm), injection-seeded Nd:YAG (Quanta Ray, GCR 5) laser at 10 Hz repetition rate. Wavelength-tunable pulses of 5 ns duration and 80 mJ/pulse energy, generated in the PDA, are frequency doubled in a KD\*P crystal. The UV (315 nm) is separated from the visible and focused (inside a vacuum chamber) in an expanding pulsed gas jet of Xe for frequency tripling down to 105 nm. The overlapping VUV and UV beams are intersected at 90° by an atomic beam of natural argon (99.6%  $^{40}\text{Ar}$ ; 0.063%  $^{38}\text{Ar}$ ; 0.337%  $^{36}\text{Ar}$ ). The ions created by 1 VUV + 1 UV photo-ionization are collected and mass-separated by a time-of-flight (TOF) mass spectrometer. Three boxcar integrators are used to detect each one of the three isotopes simultaneously. With only 10 mJ/pulse UV energy the VUV production is sufficient to detect even the least abundant  $^{38}\text{Ar}$  isotope from a natural sample. During a single scan of the CW dye laser frequency, the spectra from the three isotopes are recorded along with the  $I_2$  saturation spectrum and the etalon markers.

A single scan over 50 GHz in the VUV is shown in figure 2. The first three spectra represent the  $3p^6-3p^54s\left[\frac{1}{2}\right]_1$  transition in  $^{40}\text{Ar}$ ,  $^{38}\text{Ar}$  and  $^{36}\text{Ar}$ , respectively. The linewidth

<sup>†</sup> For notations of the hyperfine components in the iodine saturation spectrum and the calibration procedure see [9].

of the Ar resonance width is  $\sim 450$  MHz, predominantly governed by the bandwidth of the VUV source and some contribution from the residual Doppler broadening in the crossed-beam configuration. The etalon trace gives a relative frequency scale of 893.739(3) MHz per marker spacing. The scan is extended towards the nearest iodine line R67(9–4). Its ‘t’ component (denoted in figure 2 by an asterisk) is calibrated in the visible with respect to the ‘t’ hyperfine component of P61(7–3) known with  $0.000\,02\text{ cm}^{-1}$  accuracy [8]. Our measurement yields  $15\,900.190\,13(7)\text{ cm}^{-1}$  for the ‘t’ component of R67(9–4), thus setting an accurate frequency standard of  $95\,401.140\,78(42)\text{ cm}^{-1}$  in the VUV near 105 nm. The transition frequencies of the three argon isotopes observed are then determined via a procedure, involving computerized fitting of the line profiles and interpolation on the frequency scale provided by the etalon markers.

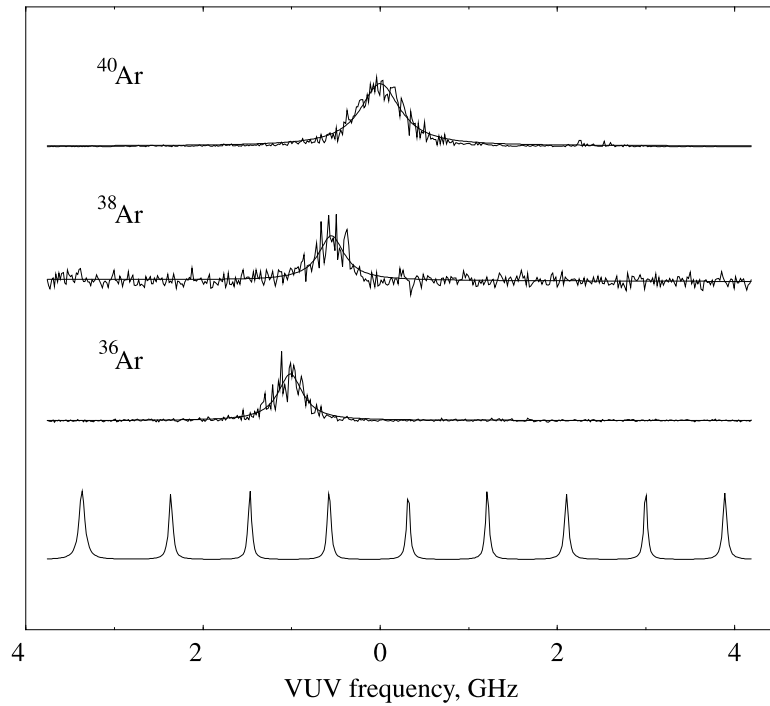
Although the absolute calibration using  $I_2$  saturation spectroscopy in the CW part of the experiment and the relation  $\nu_{\text{VUV}} = 6\nu_{\text{vis}}$  gives very good accuracy, there are several systematic error sources to be taken into account. As the geometry of the experiment allows for a slight deviation from  $90^\circ$  beam crossing, a Doppler shift may be present and must be evaluated. Increasing the velocity of the atoms by seeding Ar (10%) in an He beam at constant geometry allows us to determine the Doppler shift under the experimental conditions to be  $+20(7)$  MHz. No indication of AC Stark shift is observed for UV powers of 10 mJ/pulse (see also [1]). However, the chirp induced in the PDA has to be estimated since its contribution can be significant after the frequency up-conversion [1]. We rely on existing measurements of chirp in dye amplifiers operating on DCM [10], which set an upper limit of about 100 MHz in this wavelength region. In table 1 we summarize all contributions to the error in the measurement of the  $^1S_0-1s_2$  transition of  $^{40}\text{Ar}$ . It can be seen that the chirp generated during the amplification process is the dominant error source. A detailed quantitative evaluation of the chirp effect, as previously done for the case of helium [1], would potentially reduce the uncertainty in the measurement by a factor of three.

**Table 1.** Error budget for the  $^1S_0-1s_2$  transition frequency in  $^{40}\text{Ar}$ .

Source	Error (MHz)
Statistical $1\sigma$	20
$I_2$ calibration	12
Doppler shift	7
Chirp	$\leq 100$
Total error rms	103

Taking into account the above-mentioned remarks, the transition frequencies for the three isotopes are determined as follows:  $\nu_{40} = 95\,399.833(3)\text{ cm}^{-1}$ ;  $\nu_{38} = 95\,399.815(3)\text{ cm}^{-1}$ ;  $\nu_{36} = 95\,399.798(3)\text{ cm}^{-1}$ . To our knowledge these are the most accurate values for any transition involving the ground state of Ar so far. The best measurement for the  $1s_2$  line is the classical spectroscopic value reported by Minnhagen [5] with 15 times lower accuracy.

The presently measured transition frequency can be used to determine an improved value for the first ionization potential  $I_{3/2}$  of Ar I. In a recent study of the  $J = 4$  Rydberg series the group of Hotop [4] reported a value  $I_{3/2} = 21\,647.076(2)\text{ cm}^{-1}$  with respect to the  $3p^5 4p[5/2]_3$  level ( $2p_9$  in Paschen notation). The difference between this even-parity  $2p_9$  level and the odd-parity  $1s_2$  level (the upper level in the present experiment), follows from the work of Minnhagen [5]. We take the average of the value of Minnhagen [5] and Norlén [11] for  $2p_9$ , differing by only  $0.0011\text{ cm}^{-1}$ . Hence we deduce  $10\,062.9325(10)\text{ cm}^{-1}$  for the separation  $2p_9-1s_2$ . Combining this value with the  $^1S_0-1s_2$  transition frequency and the  $I_{3/2}(2p_9)$  from [4]



**Figure 3.** A scan over the  $^1S_0$ – $1S_2$  resonance for the three isotopes.

**Table 2.** Isotope shift analysis with respect to  $^{40}\text{Ar}$ .

A	$\delta\nu_{40-A}$ (MHz)	NMS(40, A) (MHz)	SMS = $\delta\nu_{40-A} - \text{NMS}(40, A)$ (MHz)
38	550(10)	2068	–1518(10)
36	1036(7)	4360	–3324(7)

we deduce a value for the first ionization potential  $I_{3/2} = 127\,109.842(4)\text{ cm}^{-1}$ . For the spin-orbit excited ionization limit  $I_{1/2}$  we use the fine structure splitting of  $1431.5831(7)\text{ cm}^{-1}$  for  $\text{Ar}^+$  ( $^2P_{3/2}$ – $^2P_{1/2}$ ) measured by IR spectroscopy [12], resulting in  $I_{1/2} = 128\,541.425(4)\text{ cm}^{-1}$ .

In figure 3 a simultaneous scan over the  $1S_2$  resonance in the three argon isotopes is presented along with the etalon markers spanning 8 GHz in the VUV. While in the measurement of the absolute transition frequencies the uncertainty is largely determined by systematic effects, this is not the case in a relative measurement yielding values for the isotope shifts. Hence, the uncertainty is only determined by statistical errors in the fitting procedure. The resulting isotope shifts with respect to the most abundant  $^{40}\text{Ar}$  are listed in the second column of table 2.

According to [6] the NMS of an atomic level can be calculated by the formula:

$$\Delta E_{H,L} = m_e \frac{(M_H - M_L)}{M_H(M_L + m_e)} E_H \quad (1)$$

where  $M_H$  and  $M_L$  are the masses of the heavy and light isotopes, respectively;  $m_e$  is the mass of the electron and  $E_H$  is the level energy of the heavier isotope (in our case  $^{40}\text{Ar}$ ). For the

transition of interest the shift in the transition frequency due to the NMS is

$$\text{NMS}(40, A) = \Delta E_{40,A}^g - \Delta E_{40,A}^e \quad (2)$$

where ‘g’ and ‘e’ denote the ground and excited states, respectively. The masses of the isotopes we take from [13]; the calculated values, according to equation (2) for the NMS are included in the third column of table 2. In combination with the experimentally measured isotope shifts, values for the SMS in  $3p^6-3p^54s'[\frac{1}{2}]_1$  transition are deduced and reported in the fourth column of table 2 with an accuracy that allows for future comparison with theoretical many-body calculations. As in the case of Ne [2], our measurement shows that the SMS tends to compensate for the normal mass shift in the  $np^6-np^5(n+1)s'[\frac{1}{2}]_1$  transition.

In conclusion, precision spectroscopic measurement of the  $^1S_0-1s_2$  transition in argon at 105 nm is reported along with accurate isotope shift measurements for the three stable isotopes ( $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ ,  $^{40}\text{Ar}$ ). The data provided is valuable in connecting all accurately known levels in the argon atom with the ground state and in this way an order of magnitude improvement in the ionization potentials is achieved. From the isotope shift measurements, accurate values for the SMS are deduced for this VUV transition.

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