Optics Communications 106 (1994) 59–64
North-Holland

OPTICS
COMMUNICATIONS

Wavenumber and isotropic shifts of the $^3P_0$–$^3D_1^\circ$ transition of titanium

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Received 12 August 1993; revised manuscript received 26 October 1993

The $^3P_0$–$^3D_1^\circ$ Ti I transition at 592.2 nm is investigated by means of intermodulated optogalvanic spectroscopy. This element was produced by sputtering in a hollow cathode discharge. Wavenumber and isotopic shift values were determined.

1. Introduction

In laser spectroscopy high resolution has been achieved when optogalvanic detection is combined with conventional Doppler-free techniques [1]. An important feature of the optogalvanic spectroscopy is that it allows the study of refractory elements, which can be easily detected when sputtered in a discharge. In many cases the great sensibility of this technique makes the detection possible of isotopes in a natural abundance sample.

Little information is available on the isotopic shifts (IS) of titanium. Values obtained from muonic X-ray measurements were reported by Wohlfahrt et al. [2] and, more recently, Maruyama et al. [3] and Gianfrani et al. [4] reported optical values obtained respectively from a two-step photoionization method and polarization excitation spectroscopy in a hollow cathode discharge. As pointed out in ref. [4], this element is of special interest because its isotopes are adjacent to the doubly magic ^{40}Ca nucleus and, in particular, the neutron shell of ^{50}Ti is closed.

In this work we obtained Doppler-free spectra of the $(3d^24s^2)^3P_0$–$(3d^24s4sp)^3D_1^\circ$ transition of Ti I by using intermodulated optogalvanic spectroscopy (IMOGS) [1]. As the lower level has the same parity of the $^3F_2$ ground state, electric dipole transition from the $^3P_0$ to $^3F_2$ is forbidden and therefore the $^3P_0$ level is a metastable one. As a consequence the intermodulated spectra present a large Doppler pedestal and the homogeneous signal is sitting on this pedestal. The wavenumber was measured to an accuracy of 3×10^{-7}, mainly limited by the Doppler broadening of the I_2 transitions used as reference. The IS were measured for the pairs 46–48 and 46–50 with an accuracy of 1.5×10^{-2}. This is mainly affected by the resolution imposed by the pedestal and the S/N ratio. The residual IS observed in this work are larger than previous reported values [3,4], including, in particular, a transition belonging to the same configuration [4], where we should expect similar values. These shifts may be attributed to a larger specific mass shift contribution. A theoretical analysis, based on the Hartree–Fock method, is necessary to confirm this hypothesis.

2. Experiment

The construction details of the hollow-cathode lamp were described elsewhere [5]. We used a 20 cm long glass tube with diameter of 4 cm. The lamp was sealed with argon (buffer gas) at a pressure of 1 Torr and could be operated with discharge currents up to 150 mA. It has double anodes and a titanium cathode, this one being a 10 mm long cylindric tube with internal diameter of 3 mm. The optogalvanic signal was detected through a ballast resistor with a dc-

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SSDI 0030-4018(93)E0566-X

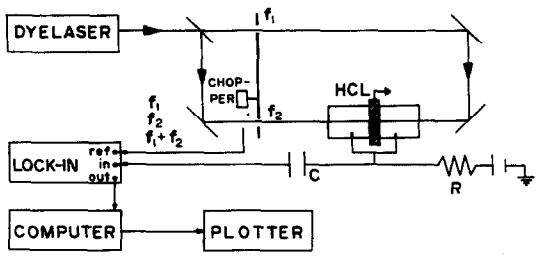

Fig. 1. Experimental setup for intermodulated optogalvanic spectroscopy (IMOGS).

blocking capacitor, using a lock-in amplifier phase referenced to a mechanical chopper.

Single-frequency radiation, with a jitter of about 1 MHz, is provided by a commericial actively stabilized ring dye laser operating with Rhodamine 6G. The laser polarization is linear and the beam is gaussian with a diameter which matches the cathode one. An Ar^+ laser was used to pump the ring dye laser. A double monochromator was used to position the laser wavelength in the region of interest and an iodine cell was then used as a reference for fine wavelength positioning and tuning. A schematic representation of the experimental setup for IMOGS is shown in fig. 1. The setup is the usual, with two counterpropagating beams of equal intensities modulated by a mechanical chopper at frequencies f_1 and f_2. The optogalvanic signal was detected by the lock-in at the sum frequency (f_1+f_2). The spectra were recorded simultaneously with the iodine Doppler broadened spectrum and with the transmission peaks of a homemade 75 MHz free-spectral-range scanning confocal Fabry–Pérot interferometer, which provides frequency calibration. Doppler-free spectra were obtained for several values of current in the discharge and laser power. The absolute wavenumber and the isotopic shifts were measured from these intermodulated spectra.

3. Experimental results

The Doppler broadened profile of the considered titanium transition was fitted to three gaussians corresponding to the isotopes 46, 48 and 50. The weak hyperfine components of the isotopes 47 and 49 were not observed here. The obtained Doppler linewidth for ^{48}Ti was about 1600 MHz (fwhm), which corresponds to a kinetic temperature of 930 K.

Figures 2 and 3 show typical intermodulated spectra for the $^3P_0$–$^3D_1^o$ titanium transition at 592.2 nm. Usually the lineshapes in spectra obtained by this technique display a homogeneous lorentzian profile

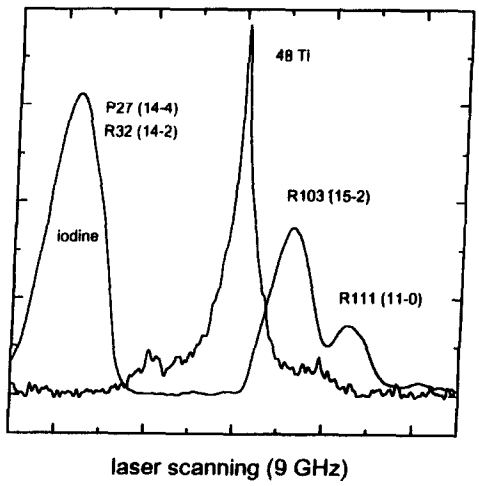

Fig. 2. The iodine Doppler broadened fluorescence spectrum in coincidence with the 592.2 nm Ti I line, obtained by IMOGS; laser frequency scanning: 9 GHz; vertical arbitrary units are different in both spectra.

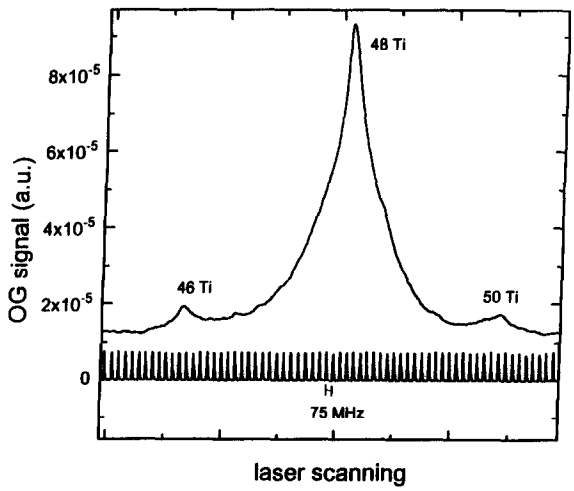

Fig. 3. Intermodulated spectrum of the 592.2 nm titanium line plotted with the 75 MHz free-spectral-range FP transmission peaks. It is observed the broad Doppler pedestal, typical of IMOGS, caused by velocity-changing collisions. The peaks corresponding to the three even isotopes are indicated.

superimposed on a large gaussian pedestal whose width depends on the Doppler linewidth. This pedestal is due to velocity-changing collisions and its shape and weight, relative to the homogenous signal, depend on the lifetimes of the levels involved in the transition as well as on the mass ratio between the colliding partners [1,6]. In our case the lower level ($^3P_0$) is a metastable one situated 8437 cm^{-1} above the ground state. We should expect a large contribution from velocity-changing collisions. In fact our intermodulated spectra exhibit a large gaussian pedestal corresponding to the isotope 48, whose width is well fitted by the Doppler linewidth, assuming the "strong collision" case (in this case the width of the pedestal is $\sqrt{2}$ times smaller than the gaussian linewidth) [1]. This pedestal is the main factor which limits the accuracy of our IS measurements. Values for the lifetimes of the levels involved in the $^3P_0$–$^3D_1^o$ Ti I transition, obtained from IMOGS and nonlinear Hanle effect, will be reported in a forthcoming paper.

3.1. Transition wavenumber

The wavenumber of the transition was measured from the intermodulated spectra, relative to the simultaneously recorded iodine Doppler broadened spectrum and the 75 MHz FP transmission peaks. The lines used as references (fig. 2) are reported as the blended lines P27 (14-4) and R32 (14-2), and the lines R103 (15-2) and R111 (11-0) in the iodine atlas of ref. (7). The corresponding wavenumbers are 16881.0867(20) cm^{-1}, 16881.2344(20) cm^{-1} and 16881.2717(20) cm^{-1}, respectively. With reference to them the wavenumber of the ^{48}Ti was found to be:

$$^{48}\text{Ti}\ (^3P_0\text{–}^3D_1^o) = 16881.201 \pm 0.002 \pm 0.003\ \text{cm}^{-1},$$

where the first error is the experimental error and the second is the calibration uncertainty. This value is in agreement with the value reported by Forsberg [8] and differs from the value obtained from the NBS table [9].

3.2. Isotopic shifts

Natural abundances of titanium are: 8.0(1) (^{46}Ti), 7.3(1) (^{47}Ti), 73.8(1) (^{48}Ti), 5.5(1) (^{49}Ti) and 5.4(1) (^{50}Ti) [10]. The IS were measured with reference to the peaks of the three even isotopes (fig. 3). Although the lines are expected to be symmetric, the presence of the unobserved hyperfine components of the odd isotopes could lead to some amount of asymmetry and, therefore, errors in the determination of the line centers. An attempt to reduce the standard deviation by calculating the center of gravity for the lines was not successful due to the presence of the Doppler pedestal.

The values found for the IS are shown in table 1. The standard deviation was obtained from a set of eight recordings. The normal mass shift (NMS) is easily calculated as being 250 MHz (46–48) and 480 MHz (46–50). The isotopic shift minus the normal mass shift is called the residual shift which is the sum of the specific mass shift (SMS) and the field shift (FS).

The IS are consistent with a pure mass shift since the calculated relative isotopic shift (RIS):

$$\text{RIS} = \frac{\text{IS}^{46\text{–}50}}{\text{IS}^{46\text{–}48}} = \frac{(M_{50} - N_{46})M_{48}}{(M_{48} - M_{46})M_{50}} = 1.9208$$

is in agreement with the experimental value of 1.95 ± 0.04 cm^{-1}. Although differences between calculated and experimental values may be indicative of the presence of FS, in practice this may not be a sensitive test because sometimes FS may obey the above expression [11]. However, deviation from the calculated value for a given line or in the experi-

Table 1
Isotopic shift values for the $^3P_0$–$^3D_1^o$ Ti I transition obtained from intermodulated optogalvanic spectroscopy (IS isotopic shift, NMS normal mass shift, RS residual shift)

Transition	Wavelength (nm)	Isotope couple	IS (MHz)	NMS (MHz)	RS (MHz)
$(3d^24s^2)^3P_0$– $(3d^24s4p)^3D_1^o$	592.2	46–48	1760(20)	250	1510(20)
		46–50	3435(25)	480	2955(25)

mental values of RIS for several lines of an element indicates the presence of FS. Table 2 shows these values for some transitions of titanium. Values reported in refs. [3] and [4] are the only published optical isotopic shifts for Ti I up to our knowledge. A large deviation from the theoretical value, and possibly a larger FS, is observed for the 625.9 nm line (table 2).

The presence of FS is usually negligible for elements with $A < 60$, but it has been observed in lighter elements like calcium [12] and oxygen [13]. The shifts reported in table 1 are more than twice the values reported in refs. [3] and [4], which are similar in magnitude. Since FS are not expected to be large compared to mass shifts for elements like titanium, we can suppose that this large difference is mainly due to SMS. One of the transitions measured in ref. [4] belongs to the same configuration as the transition in this work, according to refs. [8] and [9]. This last reference gives this configuration as doubtful, but the assignment is confirmed in the more recent work of Forsberg [8]. SMS are expected to be more sensitive to the configuration than to the term values, although there are examples of a J-dependence with a given configuration for other elements (see ref. [11] and references therein). Measurements for several transitions of a given configuration are necessary to confirm this dependence. An estimation of the SMS requires the knowledge of the wavefunctions and can be a very difficult problem for multielectronic atoms [12,14]. Configuration interaction may complicate the situation and frequently the agreement between observed and calculated SMS is not good.

The detection of isotopic pairs for various transitions with enough accuracy in the determination of the IS allows an analysis of these in terms of mass and field shift contributions, by means of a King-plot representation [11]. In ref. [4] this analysis is carried out for an uv and a red transition, indicating the presence of FS for Ti I.

In order to carry out a King-plot analysis we must measure at least three isotopes in two transitions and the modified residual shifts for these transitions are plotted against each other. The slope of the obtained straight line gives the ratio of the electronic dependent parts of the FS for the two transitions. The point at which the line crosses the vertical axes gives the difference between the electronic dependent part of the SMS. King plots may be done with the transition studied in this work and each of the two transition of ref. [4]. As the uncertainties in ref. [3] are larger, the corresponding data were not used. The modified residual shifts, taking the pair (46, 48) as reference, are shown in table 3.

Owing to the uncertainties in our measurements there is an overlap between the MRS for the 592.2 nm transition (table 3). Therefore the values determined from the King-plots are inaccurate and do not allow to draw conclusions. By plotting the MRS for the 334.3 nm transition against the ones for the 592.2 nm transition one obtains a line which has a slope of 0.5 and intersects the vertical axes at -402 MHz. In the plot for the 592.2 and 625.9 nm lines these values are 0.4 and 1297 MHz, respectively. Looking at these values of the slopes one could think that the FS, for the 592.2 nm line, would have the same direction as for the 334.3 and 625.9 nm lines of ref.

Table 2
Relative isotopic shifts (RIS) for some Ti I transitions.

Transition wavelength (nm)		RIS
334.3	ref. [4]	1.95 ± 0.02
501.6	ref. [3]	2.23 ± 0.35
504.1	ref. [3]	2.37 ± 0.44
592.2	this work	1.95 ± 0.04
625.9	ref. [4]	2.09 ± 0.02

Table 3
Values for the modified residual shifts (MRS) of some Ti I transitions, taking the couple (46, 48) as reference.

Transition wavelength (nm)		Isotope couple	MRS (MHz)
334.3	ref. [4]	46–48	408.6(5)
		46–50	423.1(3)
501.6	ref. [3]	46–48	455(60)
		46–50	574(65)
504.1	ref. [3]	46–48	356(70)
		46–50	508(60)
592.2	this work	46–48	1510(20)
		46–50	1537(13)
625.9	ref. [4]	46–48	548.7(6)
		46–50	618.4(3.5)

[4], becoming more pronounced as the transition wavelength increases. However the slopes are affected by large errors and therefore we can not conclude on the presence of FS. The uncertainties in our measurements, while not large in percentual magnitude, prevent a reasonable analysis in order to separate SMS and FS contributions by this kind of procedure.

Another way to separate SMS and FS contributions is to use a combination of optical data and X-ray data obtained from muonic atoms [11]. Wohlfart et al. [2] reported model-independent values for the changes in the mean square radius of the nuclear charge distribution, $\delta\langle r^2\rangle$, obtained by measuring the energies of muonic X-ray transitions.

The value of the plotted line for $\delta\langle r^2\rangle = 0$ can give an estimation of the SMS for the optical transition [5]. At the accuracy level of the measurements in this work, as well as in refs. [3] and [4], this separation is not possible because the uncertainties of the obtained values are larger than the values themselves. Therefore in order to determine the SMS and FS contributions by this method we should be able to measure the isotopic shifts with a greater accuracy, perhaps one or two orders of magnitude higher.

4. Conclusion

In this paper we observed with Doppler-free resolution a Ti I transition, at 592.2 nm, by intermodulated optogalvanic spectroscopy. Its wavenumber was determined with an accuracy of 3×10^{-7} and the isotopic shifts were determined for the even isotopes with an accuracy of 1.5×10^{-2}. The isotopic shifts are consistent with a pure mass shift, while there is indication of field shift for titanium in the literature. The accuracy in our IS measurements, which is mainly limited by the Doppler pedestal usually observed with the technique, prevents a satisfactory King-plot analysis in order to separate mass and field shift contributions. It prevents also an estimation of these contributions by combining optical and muonic X-ray data, taken from ref. [2]. While not large in percentual magnitude, the accuracy level achieved here should be increased by at least one or two orders of magnitude in order to allow a reasonable parametric analysis, by methods of ref. [11].

The IS values measured in this work are more than twice those for other titanium transition reported in the literature, one of them belonging to the same configuration. Since the field shift is not expected to be large for titanium, this feature can be attributed to a larger specific mass shift (SMS) for this transition, which is associated with correlations among electrons. Our results stimulate interest in the theoretical analysis of the isotopic shifts in titanium as well as on further experimental investigations. While configuration mixing may also be responsible for this larger SMS, as a theoretical analysis may confirm, this one is expected to be more sensitive to the configuration than to the term values. It may even be possible to verify a J-dependence within the configuration, as was done for other elements, if more experimental data are available.

Due to its practical advantages optogalvanic detection, combined with the various Doppler-free spectroscopic techniques, seems to be an attractive way to study this element.

Acknowledgements

The authors would like to thank N. Beverini, from the University of Pisa, Italy, for useful comments. This work was financially supported by FAPESP, CNPq, FAEP-UNICAMP, Brazil.

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