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The fifth spectrum of platinum (Pt V): Analysis of the $(5d^6 + 5d^5 6s) - 5d^5 6p$ transition array

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ARTICLE INFO

Article history:
Received 6 August 2015
Received in revised form
24 August 2015
Accepted 29 August 2015
Available online xxxx

Keywords:
Spectral line identification
Energy level
Atomic spectrum
Vacuum ultraviolet
Four times ionized platinum
Pt^{4+}

ABSTRACT

The spectrum of platinum was observed in the 300–2100 Å wavelength region. The $(5d^6+5d^5 6s) - 5d^5 6p$ transition array of four times ionized platinum, Pt V, has been investigated and 1659 spectral lines have been classified in the region of 460–1730 Å. The analysis has led to the determination of the $5d^6$, $5d^5 6s$ and $5d^5 6p$ configurations. Thirty two of 34 theoretically possible $5d^6$ levels, 45 of 74 possible $5d^5 6s$ levels and 181 of 214 possible $5d^5 6p$ levels have been established. The orthogonal operators technique was used to calculate the level structure and transition probabilities. The energy parameters have been determined by the least squares fit to the observed levels. Calculated transition probability and energy values, as well as *LS*-compositions obtained from the fitted parameters are presented.

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http://dx.doi.org/10.1016/j.adt.2015.08.002
0092-640X/

Please cite this article in press as: V.I. Azarov, R.R. Gayasov, The fifth spectrum of platinum (Pt V): Analysis of the $(5d^6 + 5d^5 6s) - 5d^5 6p$ transition array, Atomic Data and Nuclear Data Tables (2015), http://dx.doi.org/10.1016/j.adt.2015.08.002

Contents

1. Introduction and experiment 2
2. Level optimization 2
3. Analysis 2
4. Calculations 4
Acknowledgments 4
References 4
Explanation of Tables 5
Table 1. Classified lines in the $(5d^6 + 5d^5 6s) - 5d^5 6p$ transition array of Pt V 5
Table 2. Experimental and calculated energy levels (cm^{-1}) in the $5d^6$ and $5d^5 6s$ configurations of Pt V 5
Table 3. Experimental and calculated energy levels (cm^{-1}) in the $5d^5 6p$ and $5d^4 6s6p$ configurations of Pt V 5
Table 4. Fitted and calculated parameter values (cm^{-1}) in the $5d^6$, $5d^5 6s$ and $5d^4 6s^2$ configurations of Pt V 5
Table 5. Fitted and calculated parameter values (cm^{-1}) in the $5d^5 6p$, $5d^4 6s6p$ and $5d^3 6s^2 6p$ configurations of Pt V 5

1. Introduction and experiment

In 1991, Pt II lines were used to demonstrate an outstanding abundance of platinum in the chemically peculiar star χ Lupi [1]. This application renewed interest in investigation of platinum spectra. Following year, the newly observed and accurately measured low ionization laboratory platinum spectra [2] were complemented with the improved descriptions of Pt I [3] and Pt II [4]. An analysis of the third spectrum of platinum, Pt III, was reported in 1993 [5], thus extending complexity of the studied ground-state configuration of Pt ions from $5d^9$ to $5d^8$. Analyses of other Pt ions having rather simple ground-state configurations, 5d and $5d^2$, were published four and nine years later, Pt IX [6] and Pt VIII [7], respectively. Significantly more complicated platinum spectra with four to seven electrons in the outer 5d-shell, such as Pt IV, Pt V, Pt VI and Pt VII, have not been published yet.

The purpose of the present work is to study the spectrum of four times ionized platinum, Pt V, which has not been investigated before. The ion has the $5d^6$ ground-state configuration, and the lowest three configurations in both parities of Pt V are overlapping. Therefore, the spectrum is extremely complex. The current analysis became possible due to refinement in theoretical calculations utilizing the orthogonal operators approach [8–11], development of the program suite IDEN [12,13], and successful analyses of the neighboring Os VI, Os V, Os IV, Ir VI, Ir V, Au V, and Ir IV spectra [14–20].

The spectrograms for the current analysis have been photographed in the wavelength region of 300–2100 Å at the Institute of Spectroscopy, Troitsk, Russian Federation. The experimental setup was the same as described in Ref. [20]. Lines of different ionization stages could be discriminated in the spectrograms. The plates were measured on an automatic comparator controlled by the system for automatic processing of photo-spectrograms [21] and initially reduced by using impurity lines of O, C, N, Al and Si [22] present in the spectrograms.

The initial uncertainty of wavelength measurements was about 0.005 Å and 0.010 Å for the wavelengths below and higher than about 1000 Å, respectively, although it increased to about 0.015 Å locally for some sub-regions due to the lack of standards, imperfection of the plate holder and deformation of photo-emulsion, most notably at the ends of the photographic plates. We have improved the accuracy of our wavelength measurements in the course of the analysis. The final list of identified lines has standard deviations of isolated lines from the calculated positions amounting to 0.003 Å and 0.005 Å in the regions of 460–1165 Å and 1165–1730 Å, respectively, and the spectrograms contain Pt lines appeared in the second order. Although presence of these lines complicated the analysis, it helped us to improve wavelength measurements by using the secondary standards derived from the second-order lines. The lines resolved in the second order have been measured more accurately. The use of internally derived Ritz standards also contributed to improvement of the measurements.

2. Level optimization

An iterative level optimization procedure (LOP) is utilized [20] in the IDEN computer program [12,13] for the energy level system optimization. The quality of the analysis was verified by considering the uncertainty of determination of each given level with respect to the levels directly connected to it by identified transitions. If the uncertainties of experimental wavelengths are correctly estimated, the weighted mean variance (WMV) of an energy level given by Eq. (7) of Ref. [20] is considered to represent the uncertainty (squared) of the level with respect to the levels directly connected to it. Eq. (8) of Ref. [20] re-estimates the uncertainties of the involved experimental wavelengths based on their deviations from the calculated (Ritz) values and uses these uncertainties for the WMV calculation of the level. All uncertainties given in this paper are at the level of one standard deviation.

Spectral lines that are masked, blended, or having doubtful identifications are not included in the LOP. We also have excluded from the optimization all levels determined by a single transition. If the uncertainties of wavelengths of the spectral lines used in the LOP are estimated correctly, and all disturbed lines are removed from the optimization, we expect the values given by Eq. (8) of Ref. [20] to be close to or smaller than those given by Eq. (7) of Ref. [20]. We verify this relation for each level and use it as a quality check of the results of the LOP and the entire analysis.

3. Analysis

The ion under investigation belongs to the W I isoelectronic sequence. The ground-state configuration of Pt V is $5d^6$ and the lowest two excited configurations of different parities are $5d^5 6s$ and $5d^5 6p$. Only three spectra in the sequence have been investigated previously: W I, Re II, and Ir IV [24–26,20]. To obtain the initial parameters for the Pt^{4+} ion studied here, a general procedure for inter- and extrapolation of energy parameters of ions in a larger than a sequence group of neighboring elements (e.g., ions with open 5d-shell of the platinum group elements) has been employed [27]. The data on the W I and Re II spectra could not be used for extrapolation of parameters of Pt V because when the ionization stage lowers, the trends of parameters or scaling factors of their *ab initio* values become more irregular, especially when we approach the third and second spectra [8,28,29]. The published data on the Os VI, Os V, Os IV, Ir VI, Ir V, Au V, and Ir IV spectra [14–20] and our unpublished data on the Os III, Pt VI, and Pt IV spectra were the most helpful in the estimation of Pt V parameters.

In the current research we simultaneously have analyzed the Pt VII, Pt VI, Pt V, and Pt IV spectra by utilizing the same sets of spectrograms containing spectra photographed under different source conditions. This allowed us to avoid line misidentifications in the very dense platinum spectra recorded, where arrays of spectral lines belonging to different ions are overlapping, and it is

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