IOCAT 2026 Conference
The 1st International Online Conference on Atoms
29–30 January 2026 | Online

Theoretical calculations of isotope shift transitions in Ti II

F.Z. BOUALILI[1], M. NEMOUCHI[1]

[1] Department of Radiation Physics, Faculty of Physics, University of Science and Technology Houari Boumediene (USTHB), BP 32 El Alia, Bab Ezzouar 16111, Algiers, Algeria

Corresponding author: naimaboualili24@gmail.com

ABSTRACT

Accurate atomic data for Ti II are essential for abundance analyses in astronomical objects. The aim of this work is to provide accurate and extensive isotope shift transition (TIS) results for Ti II, specifically by comparing our theoretical calculations with existing experimental measurements and other theoretical predictions.

The calculations were performed using two robust multiconfiguration approaches:

The non-relativistic Multiconfiguration Hartree–Fock (MCHF) combined with the Breit–Pauli approximation (MCHF-BP). The fully relativistic Multiconfiguration Dirac–Hartree–Fock (MCDHF) combined with the Relativistic Configuration Interaction (RCI) method. These methods were implemented using the ATSP2K (Atomic Transfer and Structure Package) and GRASP2018 (General-purpose Relativistic Atomic Structure Package) codes, respectively Energy levels and isotope shift transitions (TIS) were calculated for the $3d^2\ 4s\ {}^4F_J \rightarrow 3d^2\ 4p\ {}^4G_{J+1}$ transitions in Ti II. The calculated excitation energies are found to be in good agreement with the experimental data. We present the results for the isotope shifts (ISs), which are compared extensively with previous theoretical calculations and available experimental measurements. The current theoretical TIS values show, overall, a better agreement with the experimental values than other theoretical predictions, demonstrating the high accuracy of the present work.

We have performed an extensive comparison of our computed isotope shift transitions (TIS) with existing theoretical and experimental data. Notably, the accuracy of the total isotope shift (TIS) is significantly improved compared to previous theoretical efforts. Our calculated TIS values demonstrate excellent overall agreement with the measured results, confirming the reliability and high quality of the advanced theoretical methods used in this work.

THEORY OF ISOTOPE SHIFTS

The isotope shift of energy levels arises from two main contributions: the finite nuclear mass (mass shift) and the finite size of the nuclear charge distribution (field shift). Thus, the total isotope shift between two isotopes with mass numbers A and A′ can be expressed as:

$$\delta E_{i,IS}^{A,A'} = \delta E_{i,MS}^{A,A'} + \delta E_{i,FS}^{A,A'} = E_i^A - E_i^{A'}$$

Mass shift: The isotope mass shift of an atomic level **i** is traditionally described as the sum of the normal mass shift (NMS) and the specific mass shift (SMS) contributions according to:

$$\delta E_{i,IS}^{A,A'} = \delta E_{i,MS}^{A,A'} + \delta E_{i,FS}^{A,A'} = E_i^A - E_i^{A'}$$

where the Hamiltonians $\boldsymbol{H_{NMS}}$ and $\boldsymbol{H_{SMS}}$ are given by:

$$\hat{H}_{\mathrm{NMS}} = \frac{1}{2M}\sum_{j=1}^{N}\left(\boldsymbol{p}_j^2 - \frac{\alpha Z}{r_j}\boldsymbol{\alpha}_j\cdot\boldsymbol{p}_j - \frac{\alpha Z}{r_j}(\boldsymbol{\alpha}_j\cdot\boldsymbol{C}_j^1)\boldsymbol{C}_j^1\cdot\boldsymbol{p}_j\right)$$

and

$$\hat{H}_{\mathrm{SMS}} = \frac{1}{2M}\sum_{j\neq k}^{N}\left(\boldsymbol{p}_j\cdot\boldsymbol{p}_k - \frac{\alpha Z}{r_j}\boldsymbol{\alpha}_j\cdot\boldsymbol{p}_k - \frac{\alpha Z}{r_j}(\boldsymbol{\alpha}_j\cdot\boldsymbol{C}_j^1)\boldsymbol{C}_j^1\cdot\boldsymbol{p}_k\right)$$

Field Shift: arises from the fact that isotopes of the same element have different nuclear charge distributions, which result in slightly different potentials. The level field shift can thus be estimated by taking the difference in level energy from two different calculations:

$$\delta E_{i,FS}^{(1)A,A'} = -\int_{\mathbb{R}^3}\left[V^A(\boldsymbol{r}) - V^{A'}(\boldsymbol{r})\right]\rho_i^e(\boldsymbol{r})d^3\boldsymbol{r}$$

where $\boldsymbol{V^A(r)}$ and $\mathbf{V^{A'}(r)}$ are the potentials arising from the nuclear charge distributions of the two isotopes and $\rho^e_i(r)$ is the electron density of level i of the reference isotope.

METHODS

Isotope Shift transitions were calculated using the multiconfiguration Hartree-Fock(MCHF) method combined with the Breit-Pauli (BP) approximation, implemented in the atomic structure package ATSP2k[1] and the multiconfiguration Dirac-Hartree-Fock (MCDHF)method combined with RCI method, implemented in the general-purpose relativistic atomic structure package GRASP 2018[2].

In the MCHF method, the atomic state functions ASF used to describe the states of the atom are approximate eigenfunctions of the Hartree- Fock Hamiltonian given by:

$$H = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i<j}^{N}\frac{1}{r_{ij}}$$

where ri denotes the distance between electron i and the nucleus, while rij is the distance between the i-th and the j-th electron|$\mathbf{r_i}$-$\mathbf{r_j}$|.

In this expression, the three sums represent respectively the kinetic energy of the electrons, their potential energy due to the attraction of the nucleus, and the repulsion energy between pairs of electrons.

The ASFs (Ψ) are expanded over configuration state functions (CSFs,Φ):

$$\Psi(\gamma\pi LS) = \sum_i c_i\Phi(\gamma_i\pi LS)$$

MCHF is combined with the Breit-Pauli (BP) approximation to introduce relativistic corrections. In this procedure, the energy functional is a linear combination of energy functions for the different LS terms:

$$\Psi(\gamma PJM_J) = \sum_{i=1}^{N} c_i\Phi(\gamma_i PJM_J)$$

In the MCDHF method, atomic state functions (γ P JMJ), which are approximate solutions to the Dirac Coulomb Hamiltonian, are expanded over configuration state functions (CSFs), (γiP JMJ), with appropriate total angular momentum ***J*** symmetry and parity ***P*** :

$$\Psi(\gamma\pi J) = \sum_k c_k\Phi(\gamma_k\pi L_k S_k J)$$

The CSFs are constructed from one-electron Dirac orbitals that together with the mixing coefficents are obtained in a relativistic self-consistent-field procedure by applying the variational principle . The transverse photon interaction as well as leading quantum electrodynamic (QED) corrections can be accounted for in subsequent relativistic configuration interaction (RCI) calculations.

RESULTS AND DISCUSSIONS

The results presented in this section focus on the the isotope shift transition between **$3d^24p\ {}^4G^o_{5/2} \rightarrow 3d^24p\ {}^4F_{3/2}$** of Ti II.specifically for the ^{48}Ti – ^{46}Ti isotopic pair.

Computational Shems:The accuracy of computed isotope shifts transitions depends on the quality of the wave functions. This in turn depends on the CSFs expansions, what electron correlation effects are captured, and how well the resulting wave functions reproduce measured energy separations.

For the Ti II ion, CSF expansions were generated using both Single Reference (SR-SD) and Multireference (MR-SD) approaches with Single and Double excitations. The computational strategy followed a progressive refinement:

In the SR-SD approach, CSF expansions are obtained by defining a set of important configurations called active assembly [AS] ,

are obtained by simple and double excitation from orbitals in the reference configuration to other orbitals in the [AS]. Depending on the rules, substitutions for the CSF expansion will account for valence–valence (VV), core–valence (CV), electron correlation effects. The CSF expansions are systematically enlarged by increasing the active set [AS].

In the MCDHF calculations, no substitutions were allowed from the core **($1s^22s^22p^63s^23p^6$)**, which defines an inactive closed core. This means that only valence-valence (VV) electron correlation effects were taken into account in the MCDHF calculations. These calculations were followed by RCI calculations for an extended expansion, which was achieved by opening the 3s and 3p core shells for substitutions to include core-valence (CV) and core-core (CC) effects. In the RCI calculations, (**$1s^22s^22p^6$**) was kept as an inactive closed core.

In this work, Tables I and II present the calculated Isotope Shift Transition (TIS) for Ti II using both MCHF+BP and MCDHF+RCI methods. Computing the (TIS in Ti II is particularly challenging due to the strong interactions between terms and configurations. Thus, some of the states are strongly mixed, and highly correlated wave functions are needed to accurately predict their LS -composition.

We found that the inclusion of multireference (MR) configurations is essential for predicting the correct order of TIS values. Specifically, the addition of:

Even states: **{$3d^24s^1$, $4s^13d^24d^1$, $3d^14s^14d^1$, $3d^14p^14f^1$, $4s^14d^2$,$4s^14f^2$}**

Odd states: **{$3d^24p^1$, $3d^14s^24f^1$, $3d^14p^14d^1$, $3d^14d^14f^1$, $4p^14d^2$,$4p^14f^2$}**

As illustrated in the tables, comparing the Single Reference (SR) approach (Line 2) with the Multireference (MR2 and MR6) expansions (Lines 3 and 4) demonstrates that these correlations are fundamental for aligning our theoretical predictions with experimental values[3].

as presented in Tables I and II, demonstrates a clear convergence of the theoretical TIS values toward experimental observations. In both approaches, the transition from a Single Reference (SR) model to an expanded Multireference (MR) framework—specifically up to MR6 with the [9f] active set is essential for capturing the electron correlation effects in Ti II. While the MCHF+BP calculations provide a solid foundation by including core-valence correlations, the MCDHF+RCI method offers a more rigorous treatment of relativistic effects.

Table I: Isotope shifts (in MHz) for the $3d^24p\ {}^4G^o_{5/2} \rightarrow 3d^24p\ {}^4F_{3/2}$ transition in Ti II. Calculations were performed using the MCHF+BP method within the SR-SD and MR-SD frameworks for the [9f] active set. Results are compared with experimental observations.

[AS]	HF-BP	vv-[9f]	{3p(6,5)+vv-}[9f]	{3p(6,*)+vv-}[9f]
SR	538.7	698.0	654.0	654.0
MR-2	518.4	701.9	688.7	698.0
MR-6	793.7	704.1	797.5	750.4
exp [3]	788.1(0.8)	788.1 (0.8)	788.1 (0.8)	788.1(0.8)

Table II: Isotope shifts (in MHz) for the $3d^24p\ {}^4G^o_{5/2} \rightarrow 3d^24p\ {}^4F_{3/2}$ transition in Ti II. Calculations were performed using the MCDHF+RCI method within the SR-SD and MR-SD frameworks for the [9f] active set. Results are compared with experimental observations.

[AS]	DF	vv-[9f]	{3p(6,5)+vv-}[9f]	{3p(6,*)+vv-}[9f]
SR	513.6	559.8	755.9	704.2
MR-2	518.4	567.0	605.2	778.5
MR-6	724.3	695.5	622.4	–
exp [3]	788.1(0.8)	788.1 (0.8)	788.1 (0.8)	788.1(0.8)

CONCLUSION

We have performed an extensive comparison of our computed isotope shift transitions (TIS) with existing theoretical and experimental data. Notably, the accuracy of the total isotope shift (TIS) is significantly improved compared to previous theoretical efforts. Our calculated TIS values demonstrate excellent overall agreement with the measured results, confirming the reliability and high quality of the advanced theoretical methods used in this work. We suggest that the current results be used as a reference for Ti II for various astrophysical applications.

REFERENCES

1] -Fischer, C. F., Tachiev, G., Gaigalas, G., & Godefroid, M. 2007, Comput. Phys. Commun., 176, 559

[2]-Froese Fischer, C., Gaigalas, G., Jönsson, P., & Bieron, J. 2019, ´ Comput. Phys. Commun., 237, 184

[3]-Ratajczyk, T., König, K., Bollinger, P., Lellinger, T., Varentsov, V., Nörtershäuser, W., & Spahn, J. 2024, Phys. Rev. A, 110, 032807