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# SPECTROSCOPY OF THE SPECTRAL LINES BROADENING AND SHIFT FOR HEAVY ELEMENTS IN THE BUFFER GAS

A new relativistic approach, based on the gauge-invariant perturbation theory (PT), is applied to calculating the spectral line collisional broadening and shifts for the heavy atom (thallium) in an atmosphere of the buffer inert gases. It is shown that the relation of the adiabatic broadening to collisional shift is ~ 1/55 for the system TI - He, 1/80 for the system TI - Kr and ~ 1/65 system TI-Xe, i.e. the known Folly spectral relationship is not correct in a case of the thallium hyperfine lines.

## 1. Introduction

High precision data for collisional shifts and broadening the hyperfine structure lines of heavy elements (alkali, alkali-earth, lanthanides, actinides and others) in an atmosphere of the inert gases are of a great interest for modern quantum chemistry, atomic and molecular spectroscopy, astrophysics and metrology as well as for studying a role of weak interactions in atomic optics and heavy-elements chemistry [1-15]. As a rule, the cited spectral lines shift and broadening due to a collision of the emitting atoms with the buffer atoms are very sensitive to a kind of the intermolecular interaction. Besides, calculation of the hyperfine structure line shift and broadening allows to check a quality of the wave functions and study a contribution of the relativistic and correlation effects to the energetic and spectral characteristics of the two-center (multi-center) atomic systems. From the applied point of view, the mentioned physical effects form a basis for creating an atomic quantum measure of frequency [8,9]. The corresponding phenomenon for the thallium atom has attracted a special attention because of the possibility to create the thallium quantum frequency measure. Alexandrov et al [8] have realized the optical pumping thallium atoms on the line of 21GHz, which corresponds to transition between the components of hyperfine structure for the Tl ground state. These authors have measured the collisional shift of this hyperfine line in the atmosphere of the He buffer gas.

The detailed non-relativistic theory of collisional shift and broadening the hyperfine structure lines for simple elements (such as light alkali elements etc.) was developed by many authors (see, for example, Refs. [1-14]). However, until now an accuracy of the corresponding available data has not been fully adequate to predict or identify transitions within accuracy as required for many applications. It is obvious that correct taking into account the relativistic and correlation effects is absolutely necessary in order to obtain sufficiently adequate description of spectroscopy of the heavy atoms in an atmosphere of the buffer gases. This stimulated our current investigation whose goals were to apply a relativistic PT approach [15,16] to calculating the interatomic potentials and hyperfine structure line collision shifts for some complicated (Tl, Pb) atoms in an atmosphere of the inert gases. The basic expressions for the collision shift and broadening hyperfine structure spectral lines are taken from the kinetic theory of spectral lines [2,5,7]. The exchange perturbation theory (the modified version EL-HAV) has been used to calculate the corresponding potentials (see de-

tails in [1]). Finally, new data on the oscillator strength of the forbidden transition in the lead are presented too.

## 2. Relativistic theory of spectral line shift for system "heavy atom-inert gas"

In order to calculate a collision shift of the hyperfine structure spectral lines one can use the following expression known in the kinetic theory of spectral lines shape (see Refs. [5,7]):

$$f_p = \frac{D}{p} = \frac{4\pi w_0}{kT}\int_0^\infty dw(R)\exp\left(-U(R)/kT\right)R^2 dR \qquad (1)$$

Here *U(R)* is an effective potential of interatomic interaction, which has the central symmetry in a case of the systems *A—B (*in our case, for example, *A*=Rb,Cs*; B*=He*)*; *T* is a temperature, $w_0$ is a frequency of the hyperfine structure transition in an isolated active atom; $dw(R)=Dw(R)/w_0$ is a relative local shift of the hyperfine structure line. The local shift is caused due to the disposition of the active atoms (say, the atoms of lead Pb and helium He) at the distance *R*. In order to calculate an effective potential of the interatomic interaction further we use the exchange PT formalism (the modified version EL-HAV) [1]. The relative local shift of the hyperfine structure line is defined as follows:

$$\delta\omega(R) = \frac{S_0}{1-S_0} + \Omega_1 + \Omega_2 - \frac{C_6}{R^6}\left(\frac{2}{\bar{E}_a} + \frac{1}{\bar{E}_a + \bar{E}_B}\right),$$
$$\bar{E}_{a,b} = \left(I_{a,b} + E_{1a,b}\right)/2. \qquad (2)$$

Here $S_0$ is the overlapping integral; $C_6$ is the van der Waals coefficient; *I* is the potential of ionization; $E_{1a,b}$ is the energy of excitation to the first (low-lying) level of the corresponding atom. The values $W_1$, $W_2$ in Eq. (2) are the first order non-exchange and exchange non-perturbation sums correspondingly [1,5,6]. These values are defined as follows:

$$\Omega_1 = \frac{2}{N(1-S_0)\rho_0}\sum_k{}' \frac{\langle \Phi_0'(1)\left|H_{HF}'\right|\Phi_k'(1)\rangle V_{k0}}{E_0 - E_k}$$
$$\Omega_2 = \frac{2}{N(1-S_0)\rho_0}\sum_k{}' \frac{\langle \Phi_0'(1)\left|H_{HF}'\right|\Phi_k'(1)\rangle U_{k0}}{E_0 - E_k}$$
$$\rho_0 = <\Phi_0^1(1)\left|H_{HF}'\right|\Phi_0'(1)\rangle / <\Phi_0^1(1)\left|\Phi_0'(1)\right\rangle$$

where $\acute{I}_{H}'$ is the operator of hyperfine interaction; *N* is the total number of electrons, which are taken into account in the calculation; $E_k$, $\Phi_k'(1) = F_{k_a}'(1)\varphi_{k_b}(2\ldots N)$ are an energy and a non-symmetrized wave function of state $k=\{k_a,,k_b\}$ for the isolated atoms *A* and *B*. The non-exchange matrix element of the Coulomb interatomic interaction is as:

$$V_{ko} = <\Phi'_k(1) \mid V(1) \mid \Phi'_0(1)>.$$

Correspondingly the exchange matrix element is as follows:

$$U_{k0} = \sum_{i=2}^{N}\langle \Phi_k'(1)\left|V(i)\right|\Phi_0'(i)\rangle$$

The operator *V (i)* (for example, in a case of the system Tl-He), as follows:

$$V(i) = U_{SCF}(r_{a3}) + U_{SCF}(r_{a4}) - 2U_{SCF}(R) + \frac{1}{r_{bi}} \qquad (3)$$

where $U_{SCF}(r)$ is the self-consistent field, created by the lead atomic core.

Let us return to consideration of the van der Waals coefficient $C_6$ for the interatomic *A-B* interaction. As a rule, one could use the approximate values for the van der Waals constant $C_6$. However, sufficiently large error in definition of the van der Waals constants could provide a low accuracy of calculating the interatomic potentials. The van der Waals coefficient may be written as [2,9]:

$$C_6(L,M) = C_{6,0}(L) - \frac{3M^2 - L(L+1)}{(2L-1)(2L+3)}\cdot C_{6,2}(l) \qquad (4)$$

where $C_{6,0}$ *(L)* is the isotropic component of the interaction and $C_{6,2}$ *(L)* is the component corresponding to the $P_2(cosq)$ term in the expansion of the interaction in Legendre polynomials, where the angle specifies the orientation in the space-fixed frame. The dispersion coefficients $C_{6,0}$ *(L)* and $C_{6,2}$

(*L)* may be expressed in terms of the scalar and tensor polarizabilities $\alpha_0(L;iw)$ and $\alpha_2(L;iw)$ evaluated at imaginary frequencies [9]. In particular, one may write in the helium case as follows:

$$C_{6,0}(L) = \frac{3}{\pi}\cdot\int_0^\infty \alpha_0(L;iw)\overline{\alpha}_{He}(iw)dw \qquad (5)$$

where $\overline{\alpha}_{He}$ is the dynamic polarizability of He. The polarizabilities at imaginary frequencies are defined in atomic units by the following formula:

$$\alpha_{\|}(L,M;iw) = 2\sum_{\gamma,M_\gamma}\frac{(E_\gamma - E_L)|< LM|\hat{z}|L_\gamma M_\gamma >|^2}{(E_\gamma - E_L)^2 + w^2} \qquad (6)$$

where $E_g$ is the energy of the electronically excited state $|L_g M_g >$ and the *z* axis lies along the internuclear axis. As a rule, (see, for example, Refs. [2,6-10]), the non-relativistic Hartree-Fock or the non-relativistic Kohn-Sham (KS) density functional or relativistic Dirac-Fock methods were used for calculating the corresponding wave functions. Another variant is using the relativistic wave functions as the solutions of the Dirac equations with the corresponding density functionals (Dirac-Kohn-Sham=DKS theory) and effective correlation potentials [14,15]. In our calculation we have used the relativistic PT with the optimized DKS zeroth approximation. The detailed approbation of method in studying spectra and radiative parameters the atoms is given in Refs. [15-18].

### 3. Results and conclusions

In Table 1 we present the results of our calculating energies of levels in $^{205}$Tl: experimental data and the results of the calculation method in the framework of the relativistic Hartree-Fock (RHF), the time-dependent theory of RHF (TDRHF), RMBPT-DF (see [23] and references therein) and our theory. Our data are in quite good agreement with the experimental data and data by the RMBPT-DF.

Table 1. **Energy (cm-1) levels for $^{205}$Tl: experiment and theor.data: RHF, TDRHF, RMBPT-DF and our theory (see text)**

| | RHF | TDR HF | RPT DF | Exp | Our |
|---|---|---|---|---|---|
| 7s | 21100 | 22952 | 22818 | 22786 | 22809 |
| $6p_{1/2}$ | 43909 | 50654 | - | 49264 | 49308 |
| $7p_{1/2}$ | 14282 | 15203 | - | 15104 | 15154 |
| $6p_{3/2}$ | 36670 | 42704 | 41432 | 41471 | 41501 |
| $7p_{3/2}$ | 13359 | 14224 | - | 14103 | 14145 |
| $6d_{3/2}$ | 12218 | 13130 | 13175 | 13146 | 13167 |
| $6d_{5/2}$ | 12167 | 13042 | - | 13064 | 13083 |

Table 2. **E1 amplitudes (in units $ea_B$) for Tl: Experiment and calculation data by RHF (RHF), DF plus cong. interaction (DF + CI), TDRHF, and our data**

| | L V | RHF | DF-CI | TDR HF | Our. | Exp. |
|---|---|---|---|---|---|---|
| $6p_{1/2}$-7s | L | 2.50 | 2.32 | 2.14 | 2.21 | 2.23 |
| | V | 2.00 | 1.92 | 2.15 | 2.21 | (6) |
| $6p_{3/2}$-7s | L | 3.43 | 3.10 | 2.81 | 2.82 | 2.83 |
| | V | 2.75 | 2.55 | 2.84 | 2.81 | (6) |
| $6p_{1/2}$-8s | L | 0.80 | 0.71 | 0.64 | 0.67 | 0.67 |
| | V | 0.61 | 0.56 | 0.65 | 0.66 | (3) |
| $6p_{1/2}$-8s | L | 0.86 | 0.77 | 2.63 | 0.65 | - |
| | V | 0.64 | 0.61 | 0.65 | 0.65 | |
| $7p_{1/2}$-7s | L | -8.14 | -7.52 | -7.20 | -7.25 | -7.27 |
| | V | -7.72 | -7.07 | -7.13 | -7.24 | (7) |
| $7p_{3/2}$-7s | L | -7.65 | -7.08 | -6.85 | -6.81 | -6.84 |
| | V | -7.22 | -6.86 | -6.79 | -6.80 | (7) |

In table 2 there listed the theoretical and experimental data in the amplitudes E1 transitions in thallium, in particular it is clear that methods of the RHF type without accounting correlation effects does not provide a precise description of the desired amplitude accuracy.

In Table 3 we present our theoretical results for the collisional shift $f_p$ (Hz / Torr) in a case of the pairs: TI - He, TI - Kr, Tl-Xe at T = 700K: Experiment by Chorou-Scheps-Galagher (Virginia group); Theory: A- DF method [7], B-optimized KS method with approximate estimate the constant $C_6$ [10] (see also[21,22]) and our theory. The important feature of our scheme is correct taking into account the correlation (polarization) effects with using special effective functionals from [15,19].

Table 3. **Collisional shift $f_p$ (Hz / Torr) in a case of the pairs: TI - He, TI - Kr, Tl-Xe at T = 700K: Experiment by Chorou-Scheps-Galagher;**

**Theory: A- DF method, B-optimized KS method with approximate estimate the constant $C_6$ and our theory.**

| Pair | T1-He | T1-Kr | T1-Xe |
|---|---|---|---|
| Exp. | 130 ± 30 | -490±20 | -1000±80 |
| Th:A | 155.0 | -850.0 | -1420.0 |
| Th:B | 137.2 | -504 | -1052 |
| Our: C | 135.4 | -501 | -1036 |

Table 4 shows our values (C) of the collisional shift of the hyperfine lines for thallium at different temperatures (T, K) for the systems TI-He,

Table 4. **Collisional shift $f_r$ (Hz/Torr) of the hyperfine lines for thallium at different temperatures (T, K) for the systems TI-He, Kr, Xe**

| Pair | T1-He | T1-He | T1-He |
|---|---|---|---|
| *T*, K | Th:A | Th:B | Th:C |
| 700 | 155 | 137,2 | 135,4 |
| 800 | 151 | 134,1 | 132,9 |
| 900 | 147.5 | 131,4 | 129,5 |
| 1000 | 143 | 126,2 | 124,4 |
| Pair | T1-Ar | T1-Kr | T1-Xe |
| T, K | Th:C | Th:C | Th:C |
| 700 | -112 | -501 | -1036 |
| 800 | -107 | -418 | -878 |
| 900 | -102 | -357 | -772 |
| 1000 | -94 | -304 | -694 |

Kr, Xe with alternative data from theories: A- DF approach [6] , B - optimized KS method [10]. The difference between our theoretical data and other calculation results can be explained by using different PT schemes and different approximations for calculating the wave functions. It is obvious that the using correct version of the exchange PT will be necessary for an adequate description of the energetic and spectral properties of the heavy atoms in an atmosphere of the inert gases. In Table 5 we list our ( C) calculated values for the reduced adiabatic broadening of $G_a/p$ for the thallium hyperfine line at different temperatures for the systems: TI - He. TI - Kr, TI-Xe together with results of other theories (theory A- DF approach [6] , B - optimized KS method [10]).

Table 5. **The adiabatic broadening $G_a/p$ for the thallium hyperfine line at different temperatures in the the systems: TI - He. TI - Kr, TI-Xe (results of different theories: theory A- DF approach [6] , B - optimized KS method [10].**

| T | TI-He A | TI-He B | TI-He C | TI-Kr C | TI-Xe C |
|---|---|---|---|---|---|
| 700 | 2.83 | 2.51 | 2.45 | 6.50 | 15.9 |
| 800 | 2.86 | 2.54 | 2.48 | 5.58 | 13.8 |
| 900 | 2.90 | 2.58 | 2.51 | 4.98 | 11.4 |
| $10^3$ | 2.89 | 2.56 | 2.48 | 4.28 | 10.0 |

The important aspect of the theory is an estimate of the ratio of $[G_a/p]/f_p$ . According to our data this ratio is as follows: $G_a/p / f_p \sim 1/55$ for the system TI - He, $G_a/p / f_p \sim 1/80$ for the system TI - Kr and $(G_a/p / f_p) \sim 1/65$ system TI-Xe, i.e. the known Folly relationship ($G_a/p \sim f_p$) is not correct in a case of the thallium hyperfine line.

It is obvious that the pair "Tl-inert gas" is sufficiently complicated system, for example in comparison with such a systems as the pair of "alkali atom-atom of inert gas". Obviously more detailed experimental studying as this atom as other interesting heavy atoms is very desirable.

Nevertheless, we believe that our data may be considered as very useful reference especially if there will be performed the further measurement of the temperature dependence for the collisional shift and adiabatic broadening parameters in a wide interval of the thermodynamical parameters.

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## SPECTROSCOPY OF THE HYPERFINE LINES SHIFT FOR HEAVY ELEMENTS IN THE BUFFER INERT

**Abstract**

A new relativistic approach, based on the gauge-invariant perturbation theory (PT), is applied to calculating the spectral line collisional broadening and shifts for the heavy atom (thallium) in an atmosphere of the buffer inert gases. It is shown that the relation of the adiabatic broadening to collisional shift is ~ 1/55 for the system TI - He, 1/80 for the system TI - Kr and ~ 1/65 system TI-Xe, i.e. the known Folly spectral relationship is not correct in a case of the thallium hyperfine lines.

**Key words:** spectral lines shift, broadening, heavy elements, buffer gas, relativistic theory

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## СПЕКТРОСКОПИЯ СДВИГОВ ЛИНИЙ СВЕРХТОНКОЙ СТРУКТУРЫ ТЯЖЕЛЫХ ЭЛЕМЕНТОВ В БУФЕРНОМ ГАЗЕ

**Резюме**

Новый релятивистский подход, основанный на калибровочно-инвариантной теории возмущений, применен для расчета столкновительного сдвига и адиабатического уширения спектральных линий тяжелого атома (таллий) в атмосфере буферных инертных газов. Показано, что отношение адиабатического уширения к столкновительному сдвигу составляет ~ 1/55 для системы TI-He, ~ 1/80 для системы TI-Kr и ~ 1/65 для системы TI-Xe, что подтверждает некорректность известного спектрального отношения Фоли в случае линий сверхтонкой структуры таллия.

**Ключевые слова:** сдвиг, уширение спектральных линий, тяжелые элементы, буферный газ, релятивистская теория

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# СПЕКТРОСКОПІЯ ЗСУВІВ ЛІНІЙ НАДТОНКОЇ СТРУКТУРИ ВАЖКИХ ЕЛЕМЕНТІВ В БУФЕРНОМУ ГАЗІ

**Резюме**

Новий релятивістський підхід, який базується на калібрувально-інваріантної теорії збурень, застосовано для розрахунку зсуву та адіабатичного уширення за рахунок зіткнень для важкого атома (талій) в атмосфері буферних інертних газів. Показано, що відношення адіабатичного уширення для зсуву за рахунок зіткнень складає ~ 1/55 для системи TI -He, 1/80 для системи TI-Kr та ~ 1/65 для системи TI-Xe, що підтверджує некоректність відомого спектрального відношення Фолі у випадку надтонких ліній талія.

**Ключові слова:** зсув, уширення спектральних ліній,, важкі елементи, буферний газ, релятивістська теорія