PECULIARITIES OF 221.1-NM Tl I ($6s^26p\ ^2P^0_{1/2} - 6s6p^2\ ^4P_{1/2}$) SPECTRAL LINE EXCITATION AT ELECTRON-ATOM COLLISIONS

H.G. BOHACHOV, E.YU. REMETA

Institute of Electron Physics, Nat. Acad. of Sci. of Ukraine
(21, Universytets'ka Str., Uzhgorod 88017, Ukraine; e-mail: dep@mail.uzhgorod.ua)

PACS 34.80.Dp
©2010

The excitation function for the 221.1-nm spectral line of a thallium atom originating from the $6s6p^2\ ^4P_{1/2}$ level at electron-atom collisions has been studied in the energy range from the excitation threshold to 16 eV and with an energy spread of about 0.7 eV. A number of structural features related to the autoionizing states and the shape resonances has been found in the excitation function above the ionization threshold.

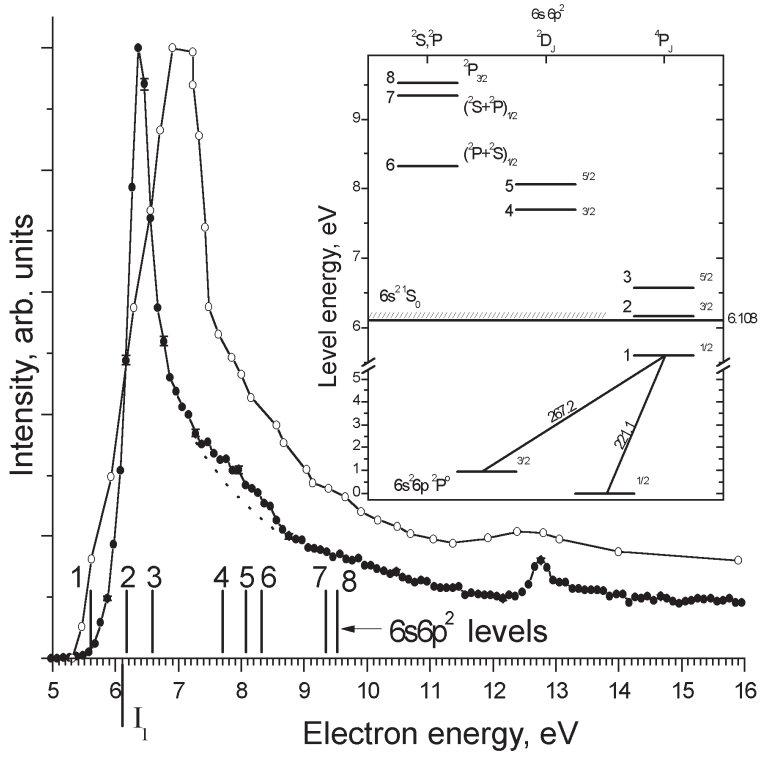
When discrete atomic levels located up to the ionization threshold are excited by electrons with the energy above this threshold, the role of autoionizing states (AISs) is crucial. The excitation process behavior becomes complicated as a result of the intensive interaction between levels of the discrete and continuous spectra, as well as owing to the strong interaction of levels belonging to different configurations between themselves. It can give rise to the effective formation of electron configurations with a few excited electrons and to the excitation by the resonant mechanism and owing to the so-called post-collision interaction (PCI). Certainly, the indicated mechanisms of population compete with the known mechanism of level population by means of cascade radiative transitions from higher levels.

The ground state of a thallium atom $^2P^0_{1/2}$ belongs to $6s^26p$ configuration which also possesses a metastable component $^2P^0_{2/2}$ with an energy of 0.966 eV. The excitation of a valence $6p$-electron produces a system of ordinary excited levels of a thallium atom which converge to the ionization threshold at 6.108 eV, the latter corresponding to the ground level $6s^2\ ^1S_0$ of a single-charged thallium ion. The emission spectrum of Tl I, which is generated at transitions from such levels onto the ground one (except for the 535.0-nm resonant line produced by the $7s\ ^2S_{1/2}$ level), lies in the ultra-violet spectral range, whereas various combinations of excited levels produce lines in the visible and infra-red spectral ranges.

The transfer of one of the $6s$-electrons to the valence $6p$-subshell gives rise to the formation of electron configuration $6s6p^2$, which is associated with a group of eight levels. In conventional notations of the LS-coupling scheme, these are levels $^4P_{1/2,3/2,5/2}$, $^2P_{1/2,3/2}$, $^2D_{3/2,5/2}$, and $^2S_{1/2}$ (see the inset in Fig. 1, where the scheme of levels 1 to 8 of $6s6p^2$ configuration is depicted, as well as their identification according to the data of work [1]). Generally speaking, the application of LS-scheme notations for those levels is conditional, because, according to the results of calculations [1], they are better described in the jj-coupling scheme. So, the relativistic effects are rather substantial in this atom and can therefore lead to intensive radiative transitions between levels with different multiplicities, i.e. with the spin change $\Delta S \neq 0$. Except for the lowest level $6s6p^2\ ^4P_{1/2}$, which lies by approximately 0.5 eV lower than the ionization potential, each level indicated above lies in the continuum and, hence, it can decay with electron ejection, i.e. through autoionization. The levels of $6s6p^2$ configuration were found with the use of various experimental techniques. For instance, the levels optically coupled with the ground state were found, while studying the photoabsorption spectra of thallium vapor in the near vacuum ultra-violet (VUV) range [1, 2]. The others were found from the emission spectra of arc discharge [3] and the spectra of ejected electrons which are generated at electron-atom collisions [4].

Theoretical calculations of the energies of low-energy AISs were carried out in various approximations. For instance, the Hartree–Fock (HF) method was used in works [1, 4] , and the Dirac–Fock one, which takes the configuration hybridization into account to a certain extent, was considered in work [5]. The AIS widths were not calculated.

Emission lines, which are a result of transitions from the lowest level ($6s6p^2\ ^4P_{1/2}$) onto the levels $^2P^0_{1/2,3/2}$ of the ground $6s^26p$ configuration, have wavelengths of 221.1 and 267.2 nm, respectively. In work [3], some information was obtained concerning the radiative decay



Excitation functions of the 221.1-nm spectral line: our data (solid circles) and the data of work [6] (hollow circles). A simplified diagram of levels of $6s6p^2$ configuration is depicted in the inset

of AIS of $6s^26p$ configuration. The electron excitation of the 221.1- and 267.2-nm spectral lines of a thallium atom was studied in work [6] with the help of an electron beam and a cell with thallium vapor. The absolute excitation cross-sections were determined for those lines. The maximum cross-section turned out rather considerable (1.59×10^{-16} cm^2) for the line at 221.1 nm and 65 times as low for the line at 267.2 nm.

This paper reports the results of a careful research dealing with the excitation of the 221.1-nm Tl I spectral line, by using the method of intersecting electron and atom beams. In general, the experimental installation was similar to that described by us earlier [7]. It should only be noted that, in our experiments, a three-anode electron gun with a ribbon-type cathode was used, which allowed electron beams with an energy spread of 0.7 eV – i.e. almost twice as narrow as in work [6] – to be obtained. To extract the 221.1-nm spectral line, a Seya–Namioka monochromator with a concave toroidal replica grating with meridional and sagittal curvature radii of 500 and 333 mm, respectively, covered with an aluminum layer and protected by a magnesium fluoride layer was used. A commercial solar-blind photomultiplier FEU-142 with a Cs_2Te-photocathode (the spectral sensitivity range was 110–320 nm) was used as a detector. Measurements were carried out with the use of an automated system for the data accumulation constructed on the basis of an IBM-compatible personal computer.

In Figure, the measured excitation function (EF) for the 221.1-nm Tl I line is depicted. The EF was measured for the electron energies E ranging from the excitation threshold to 16 eV with a step of 0.1 eV. Attention is attracted by rather a complicated shape of the obtained EF with two sharp pronounced peaks: the major one is located at an energy of about 6.3 eV near the excitation threshold, and an additional one is located at an energy of about 12.7 eV and possesses an amplitude by an order of magnitude smaller (∼6% of the major peak amplitude). Besides those peaks, there exists a broad peculiarity–an appreciable deviation from the monotonous decay–in the energy range from 7 to 9 eV. It is worth noting that the half-height widths of the indicated peaks correspond to the energy spread of exciting electrons and amount to about 0.7 eV (see above). This circumstance allows us to suppose that the peaks may have a resonance origin, i.e. they are related to the for-

mation and the decay of short-lived states of a negative thallium ion. The positions of the ionization potential I_1 and the levels of $6s6p^2$ configuration are marked by vertical dashes in the figure.

Figure also exposes the data of early EF measurements for the 221.1-nm line [6] which were carried out with the use of an electron beam with an energy spread of 1.5 eV. A comparison between two curves testifies to their similarity and unambiguously demonstrates a direct dependence of peak widths on the energy homogeneity of an electron beam, which is an additional argument in favor of the resonance origin of the structures observed. It is evident that at least the major peaks in both curves have a "resonance" character – of course, making a correction for the energy spread of electrons in the beam. The spike-like shape of EF for this spectral line, in opinion of the authors of work [6], can be explained by the fact that the quartet level $6s6p^2\ {}^4P_{1/2}$, which is initial for the 221.1-nm line, is excited due to the exchange process with spin variation. A spike-like form of EF is known (see pp. 444–454 in work [8]) to be characteristic of such excitation processes, because such an exchange mechanism predetermines a quick decrease of the excitation cross-section with growth of the collision energy (of the order of E^{-3}). In our opinion, the spin change by 1 can be associated in this case not only with the exchange process, but with substantial relativistic (spin-orbit) effects as well. First of all, it concerns the ground state of an atom. As to the second peak, it is worth noting that the curve in work [6] (see Figure) also demonstrates a weakly pronounced structure at energies of $12 - 14$ eV which may probably correspond to the additional peak in our curve.

Let us analyze, at a qualitative level, the probable nature of the observed EF features. It is determined by a characteristic feature in the structure of the thallium atom spectrum: the autoionization region from I_1 to 9.6 eV includes only the levels of $6s6p^2$ configuration, whereas the highly excited levels are located in the vicinity of 13 eV.

In the interval from the initial level to I_1, the states of one-electron excitation $6s^2nl\ {}^2L$ lie. The contribution of a cascade population of the initial level of the line by transitions from those states cannot be substantial in the regions of the first peak and the 7–9-eV feature, because such processes are inefficient owing to a "nonresonance" character of level excitation [9] and the two-electron type of transitions. Hence, the major peak and the feature at energies 7–9 eV are associated with levels of $6s6p^2$ configuration only.

In this case, the resonance mechanism of initial level population seems to be the most probable. Since the major peak is localized just above the level (2) $6s6p^2\ {}^4P_{3/2}$, it is reasonable to suppose that it is coupled with this AIS. In the region of this peak, the influence of $6s6p^2\ {}^4P_{3/2}\,\varepsilon\ell$ ($\ell \geq 1$) shape resonance, i.e. the negative ion state, is possible. It is formed at the excitation of AIS (2) $6s6p^2\ {}^4P_{3/2}$. This resonance effectively, almost without changing the characteristics of "parent" AIS (the total momentum $\Delta J = 1$, the parity $\Delta\pi = 0$, the total orbital momentum $\Delta L = 0$, and the total spin momentum $\Delta S = 0$), decays into the initial level (1) – $6s6p^2\ {}^4P_{1/2} + \varepsilon'\ell'$ [10]. The resonance that is based on the AIS (3) $6s6p^2\ {}^4P_{5/2}$ at about 6.5 eV seems to be less probable, since its total momentum changes by two at the decay.

The EF peculiarity in the energy range from 7 to 9 eV can be associated with several shape resonances. The latter are formed at exciting the doublet AISs of the given $6s6p^2$ configuration and effectively decay onto the initial level. The quantum numbers change at that as follows: ${}^2D_{3/2}$, ${}^2D_{5/2}$ (levels 4 and 5) ($\Delta J = 1$ and $\Delta J = 2$, $\Delta\pi = 0$, $\Delta L = 1$, $\Delta S = 1$), $60\ {}^2P_{1/2} + 35\ {}^2S_{1/2}$ (level 6) ($\Delta J = 0$, $\Delta\pi = 0$, $\Delta L = 0$ and $\Delta L = 1$, $\Delta S = 1$), $58\ {}^2S_{1/2} + 40\ {}^2P_{1/2}$ (level 7) ($\Delta J = 0$, $\Delta\pi = 0$, $\Delta L = 1$ and $\Delta L = 0$, $\Delta S = 1$), ${}^2S_{1/2}$ (level 8) ($\Delta J = 1$, $\Delta\pi = 0$, $\Delta L = 1$, $\Delta S = 1$). The closeness of level energies in groups (4–6) and (7,8), together with a substantial nonmonoenergeticity of electrons, seems to result in that the smeared manifestation of those resonances is observed. An improvement of electron monoenergeticity may resolve the details of this resonance structure.

It is worth noting that the effect of configuration mixing may play a large role in the processes of initial level excitation (see subsections 2.2 and 3.4 in monography [11]). For instance, the EF peculiarity in the interval of 7–9 eV can emerge due to a mixing of doublet levels ${}^2P_{1/2}$ and ${}^2S_{1/2}$ in $6s6p^2$ configuration and the initial level ${}^4P_{1/2}$ (see the diagram of levels 1–8 of this configuration in the inset of Fig. 1).

The analysis of the origin of the second peak is much more complicated. First, a state (states) that can induce it must be identified. Second, the probable mechanisms of its formation have to be indicated. This peak is evidently associated with levels of highly excited electron configurations. In work [4], the AIS with an energy of about 12.7 eV was found (the corresponding line in the ejected electron spectrum should be observed at an energy of about 6.6 eV). In the same work, the level energies for electron configurations of two types – $6s6p7p$, $6s6p7s$, $6s6p6d$ ($6s$-excitation) and $5d^96s^26p^2$

($5d$-excitation) – were calculated by applying the HF method. They were used for the identification of ejected electron spectra. The energies of those levels fall within the interval from 11 to 18 eV. The majority of lines identified in work [4] were attributed to AISs that are observed in photoabsorption spectra [1, 2]. The analysis of calculation data evidences the absence of a level among them which could be related to the structure in our EF at 12.7 eV.

In our opinion, the sought level could belong to $5d^{10}6p^3$ configuration ($^4S^0_{3/2}$ is probably its lowest level). Note that the excitation of level $^4S^0_{3/2}$ from the ground state occurs by means of the exchange mechanism, as it does in the case of the excitation of the initial level $^4P_{1/2}$. But here, we have a two-electron transition, contrary to the one-electron one in the latter case. Therefore, the EF of level $^4S^0_{3/2}$ can have a spike-like form, whereas the peak can be much less by magnitude than the first one (see above). In other words, the relation between the peak amplitudes may testify to a difference between contributions made by one- and two-electron transitions.

$5d^{10}6p^3$ configuration was also considered in work [4] (see the references therein). Though the authors of work [4] made calculations within the HF method for a variety of electron configurations (see above), $5d^{10}6p^3$ configuration was not considered theoretically. However, on the basis of the comparison made between their experimental data and the results of other authors for Ga and In atoms, the authors of the cited work expressed an expectation that all the five levels ($^4S^0$, $^2P^0$, $^2D^0$) of this configuration produce lines in the spectra of ejected electrons at energies above 6 eV (it corresponds to the level energy higher than about 12.1 eV).

We estimated the averaged energy of $6p^3$ configuration using the modified Rydberg formula [7]. Choosing the electron configuration of Tl^{3+} ion in the ground state as a core, the following expression can be used to evaluate this energy:

$$E([5d^{10}]6p^3) = I_1 + I_2 + I_3 - \frac{3(Z_c - 2\sigma^{6p}_{6p})^2}{(6-\delta_{6p})^2}R \ ,$$

where $[5d^{10}]$ is a symbolic notation of the core, $Z_c = 3$ is its charge, $R = 13.6058$ eV is the Rydberg constant, σ^{6p}_{6p} is the two-electron screening constant, δ_{6p} is the quantum defect, and the ionization potentials are $I_1 = 6.1083$ eV, $I_2 = 20.43$ eV, and $I_3 = 29.85$ eV [12]. The quantum defect δ_{6p} was found, knowing an energy of 9.1789 eV for the term $[5d^{10}]6p\,^2P^0$ of Tl^{2+} ion obtained by averaging over states of the fine structure taken from work [13] and using the formula

$$E([5d^{10}]6p\,^2P^0) = I_1 + I_2 + I_3 - \frac{(Z_c)^2}{(6-\delta_{6p})^2}R \ .$$

The screening parameter σ^{6p}_{6p} was found, knowing an energy of 15.6704 eV for the AIS $[5d^{10}]6p^2\ ^3P$ of Tl^+ ion obtained by averaging over states of the fine structure taken from work [13] and using the formula

$$E([5d^{10}]6p^2\,^3P) = I_1 + I_2 + I_3 - \frac{2(Z_c - \sigma^{6p}_{6p})^2}{(6-\delta_{6p})^2}R \ .$$

The corresponding calculated values are $\sigma^{6p}_{6p} = 0.255$ and $\delta_{6p} = 3.566$. Then the energy is $E([5d^{10}]6p^3) = 13.67$ eV. Although it is by 1 eV higher than the energy of the peculiarity found by us in the EF, nevertheless, this allows the given level to be regarded as responsible for the initial level population.

A possible channel of formation of the 12.7-eV peculiarity is a cascade population of the initial level of the 221.1-nm line. It is clear that, among the AISs that were observed in work [4], one can hardly find a suitable level, because the levels, which manifest themselves in electron spectra, do not do it in radiation. Hence, it must be a level which is metastable with respect to a decay with the electron ejection. It should be noted that, in accordance with the selection rules for the electric dipole transition ($\Delta J = 1$, $\Delta\pi = 1$, $\Delta L = 1$, $\Delta S = 0$), the radiative transition from AIS $6p^3\ ^4S^0_{3/2}$ onto the $6s6p^2\ ^4P_{1/2}$ level is allowed, whereas its electron decay into the ground state $6s^2\ ^1S_0 + \varepsilon\ell$ of Tl^+ ion seems ineffective. Really, such a transition is three-electron and, according to severe selection rules for the total momentum and the parity, it is accompanied by the changes of the total orbital momentum by 1 and the system spin by 0, whereas the orbital momentum of the ejected electron acquires a value of 1. All that allows such a decay to be considered rather improbable, i.e. with a small autoionization width.

The best confirmation of the hypothesis of a cascade population of the initial level would be the direct observation of the emission line associated with this transition. Since the energy, at which the additional spike-like peak was observed, amounted to 12.7 ± 0.2 eV, it is easy to determine that the spectral interval, where such radiation emission is to be observed, lies approximately between 169.9 and 179.8 nm. However, a careful study of spectra did not reveal any presence of appreciable emissions within the specified range at electron energies of $12 - 16$ eV. Only at energies above 20 eV, there appear the spectral lines near to this spectral range which are

located at 179.3, 181.5, and 182.8 nm, but they belong to a single-charged thallium ion. Therefore, it becomes clear that the appearance of the peculiarity at 12.7 eV is not connected with cascade transitions.

Let us analyze a probable mechanism of population of the initial level (1) in a vicinity of the other peak due to PCI. It is known that PCI can lead to the appearance of a maximum in the EF owing to the excitation and the electron decay of the corresponding AIS. The energy position of such a maximum is shifted with respect to the AIS position toward higher energies. In our case, the initial stage of this mechanism is the electron decay of AIS $6p^3\ ^4S^0_{3/2}$ (with the energy E_a), which was excited by an incident electron with energy E, into the ground state of the ion, $6s^2\ ^1S_0$. As was indicated above, the states of all three electrons change at that, $\Delta\ell_1 = \Delta\ell_2 = 1$ and $\Delta\ell_3 = 0$, and the system spin changes by 0, 1. Therefore, the autoionization width of this state can be narrow, i.e. this state is long-living, being metastable. Then the PCI occurs. It is determined by the interaction between the ejected electron (with the energy $\varepsilon \approx 6$ eV and $\ell_{ej} = 1$) and the scattered one (with the energy $E_1 = E - E_a$), on the one hand, and the ion (in the $6s^2\ ^1S_0$ state), on the other hand. This may result in populating the initial $6s6p^2\ ^4P_{1/2}$ level (with the binding energy $E_b \approx 0.5$ eV) [14, 15] owing to the capture of the scattered electron by the ion. One can see that the states of two electrons in the atom and the energy of the ejected electron in the continuous spectrum $\tilde{\varepsilon} = \varepsilon + E_1 + E_b$ must change in this case. Hence, three or two electrons take part at every stage of the process, which evidently gives rise to a low probability of AIS electron decay and, in turn, to a low probability of this mechanism. By analogy, the mechanism of PCI, where AISs (2) and (3) of $6s6p^2$ configuration are engaged, seems also to be improbable at the formation of the first dominating peak.

The low efficiency of the cascade and PCI mechanisms allows us to assert that the influence of only the shape resonance $6p^3\ ^4S^0_{3/2}\tilde{\varepsilon}\tilde{\ell}$ ($\tilde{\ell} \geq 1$) is possible in the second-peak region. It is formed at the two-electron excitation of AIS $6p^3\ ^4S^0_{3/2}$, which consists in a transition of both electrons from the subvalence $6s$-subshell. This resonance also effectively decays into $6s6p^2\ ^4P_{1/2} + \tilde{\varepsilon}'\tilde{\ell}'$ [10]. In this case, the variations of quantum numbers of "parent" AIS correspond to the selection rules for a dipole radiative transition, as was indicated above.

Conclusion

The peculiarities at energies of 6.3, 7–9, and 12.7 eV on the function of the electron excitation of the 221.1-nm spectral line of a thallium atom, which is related to the level $6s6p^2\ ^4P_{1/2}$, have been detected and qualitatively analyzed. Two peak-like maxima at the excitation threshold and at 12.7 eV were associated with shape resonances which are formed at the excitation of AISs $6s6p^2\ ^4P_{3/2}$ and $6p^3\ ^4S^0_{3/2}$, respectively. The energy of the latter level was estimated by the modified Rydberg formula. The analysis (on the basis of selection rules) of the initial level $6s6p^2\ ^4P_{1/2}$ population by means of the radiative cascade transition from the level $6p^3\ ^4S^0_{3/2}$ and the PCI process that engages the levels $6p^3\ ^4S^0_{3/2}$ and $6s6p^2\ ^4P_{3/2,5/2}$ demonstrated a low efficiency of those excitation channels. A considerable deviation from the monotonous decay of EF within the energy interval 7–9 eV was associated with shape resonances which are formed at the excitation of doublet AISs of $6s6p^2$ configuration. A more detailed specification of the EF structure at those energies can be obtained by enhancing the monoenergeticity of exciting electrons. A large role of the effect of strong configuration mixing in the processes of thallium atom initial level excitation was emphasized.

The authors are sincerely grateful to the Yu.I. Roman (IEP of the NAS of Ukraine) for his valuable advices concerning the methods of operation with metallic thallium and to I.Yu. Yurova (Saint-Petersburg University, Russia) for her assistance in obtaining a copy of paper [5]. The work was partially supported by the INTAS grant No. 03-51-4706.

1. J.-P. Connerade and M.A. Baig, J. Phys. B **14**, 29 (1981).
2. M.G. Kozlov, *Absorption Spectra of Metal Vapors in Vacuum Ultraviolet* (Nauka, Moscow, 1981) (in Russian).
3. H.E. Clearman, J. Opt. Soc. Am. **42**, 373 (1952).
4. C. Back, V. Pejcev, K.J. Ross, and M. Wilson, J. Phys. B **16**, 2413 (1983).
5. V.A. Zilitis, Opt. Spektrosk. **88**, 192 (2000).
6. L.L. Shimon, E.I. Nepiipov, N.A. Gatsyuk, and I.P. Zapesochnyi, Opt. Spektrosk. **32**, 1040 (1972).
7. H.G. Bohachov and E.Yu. Remeta, Opt. Spektrosk. **86**, 727 (1999).
8. S.E. Frish, *Optical Spectra of Atoms* (Fizmatgiz, Moscow-Leningrad, 1963) (in Russian).
9. L.L. Shimon, E.I. Nepiipov, and I.P. Zapesochnyi, Ukr. Fiz. Zh. **17**, 1955 (1972).
10. H. Bohachov and E.Yu. Remeta, in *Abstracts of the 24-th International Conference on Photonic, Electronic, and Atomic Collisions* (Rosario, Argentina, 2005), p. Mo040.
11. R. Karazija, *Introduction to the Theory of X-Ray and Electronic Spectra of Free Atoms* (Plenum Press, New York, 1996).

12. A.A. Radtsig and B.M. Smirnov, *Parameters of Atoms and Atomic Ions: A Handbook* (Energoatomizdat, Moscow, 1986) (in Russian).

13. Ch.E. Moore, in *Atomic Energy Levels, Vol. 3* (Circular of the NBS 467, Washington: USA, 1958), p. 55.

14. H.G. Bohachov and E.Yu. Remeta, Opt. Spektrosk. **103**, 733 (2007).

15. H.G. Bohachov and E.Yu. Remeta, Ukr. Fiz. Zh. **53**, 126 (2008).

Received 24.12.09.
Translated from Ukrainian by O.I. Voitenko

ОСОБЛИВОСТІ ЗБУДЖЕННЯ СПЕКТРАЛЬНОЇ ЛІНІЇ 221,1 НМ Tl I ($6s^26p\ ^2P^0_{1/2} - 6s6p^2\ ^4P_{1/2}$) В ЕЛЕКТРОН-АТОМНИХ ЗІТКНЕННЯХ

Г.Г. Богачьов, Є.Ю. Ремета

Р е з ю м е

Для спектральної лінії атома талію 221,1 нм, що виходить з рівня $6s6p^2\ ^4P_{1/2}$, досліджено функцію збудження при зіткненнях атомів з електронами в області енергій від порога збудження до 16 еВ та розкидом по енергії ∼0,7 еВ. Вище потенціалу іонізації на функції збудження знайдено низку особливостей, пов'язаних з автоіонізаційними станами та резонансами форми.