Theoretical and experimental study of some basic processes in He-TII and Ne-TII plasma – asymmetric charge transfer, Penning ionization and diffusion

K A Temelkov, N K Vuchkov, R P Ekov and N V Sabotinov

Metal Vapour Lasers Laboratory, Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria

E-mail: temelkov@issp.bas.bg

Abstract. The diffusion coefficients of thallium and iodine atoms in a binary system with helium and neon are calculated on the basis of 12-6 Lenard-Jones and rigid sphere models. Cross-sections and rate constants for thermal energy charge transfer into some Tl+ and I+ excited states are theoretically and experimentally obtained for a gas discharge in He-TII and Ne-TII mixtures. Cross-sections and rate constants for Penning ionization into Tl+ and I+ ground and excited states are calculated for Penning collisions with the He and Ne metastable atoms. Since the characteristic constants studied depend on the gas temperature, the radial gas temperature distribution is also calculated through solving the heat conduction equation.

1. Introduction

One of the main problems in plasma physics is to determine the characteristic constants for basic processes in plasma, such as asymmetric charge transfer, Penning ionization, diffusion and radiation transitions. There is continuous interest in these processes, because they play an important role in a large variety of phenomena and devices in gaseous discharges, laser physics, plasma technologies, gas-discharge mass spectroscopy, absorption and emission spectroscopy, and plasma in general.

The diffusion coefficient $D_{12}$ of a binary gas system containing particles of sort 1 and sort 2 is a function of the potential of interaction between these particles. Following [1], the diffusion coefficient $D_{12}$ for the rigid sphere and 12-6 Lenard-Jones models, respectively, are expressed as follows:

$$D_{12}^1 = \frac{\mu_r T_g^3}{\mu^2 \cdot p \cdot d_{12}^2} \quad D_{12}^2 = \frac{T_g^3}{\mu_r \cdot p \cdot \sigma_{12}^2 \cdot \Omega_D \left( \frac{kT_g}{\varepsilon_{01}} \right)}$$ (1)

where $\mu_r$ is the reduced mass of the two collision partners in amu, $p$ is the gas pressure in atm, $T_g$ is the gas temperature in K, $d_{12}$ is the sum of atomic radii of the interacting particles in Å, $\sigma_{12} = 0.5*(\sigma_1 + \sigma_2)$ is the inter-atomic distance in Å where the potential energy is zero, $\varepsilon_{012} = \sqrt{\varepsilon_{01} \cdot \varepsilon_{02}}$ is the potential well depth, $\Omega_D$ is collision integral. In the case of self-diffusion, $\sigma_{12} = \sigma_1 = \sigma_2$ and $\varepsilon_{012} = \varepsilon_{01} = \varepsilon_{02}$. The two parameters of the Lenard-Jones potential are estimated using the following empirical formulae...
\[ \frac{\varepsilon_k}{k} = 0.75 \cdot T_c \] and \[ \sigma = \frac{5}{6} V_c^{\frac{1}{3}}, \] where \( T_c \) and \( V_c \) are critical temperature and volume, respectively, and \( k \) is the Boltzmann constant.

The thermal energy charge transfer reaction into excited states occurs according to the following scheme \( A^+ + B \rightarrow A + B^+ + \Delta(\infty) \), where \( A^+ \) denotes the rare gas ions in ground state, \( B^+ \) is the excited ion state to which the atom-target is ionized and excited, and \( \Delta(\infty) \) is the infinite separation energy defect \( \Delta(\infty) = E(A^+) - E(B^+) \). As in [2], the cross section \( \sigma_{th} \) may then be calculated using the following expression:

\[ \sigma_{th} = \frac{4\pi e}{v_r} \mu_r \exp(-G) \left[ 1 - \exp(-G) \right], \tag{2} \]

where \( v_r \) is the relative velocity in cm/s, \( \alpha \) is the dipole polarizability of the neutral partner in cm\(^3\), \( \mu_r \) is the reduced mass of the system in g, \( G \) is a parameter that depends on the infinite separation energy defect \( \Delta(\infty) \), and \( e \) is the electron charge - 4.8029\( \times 10^{-10} \) CGSE (cm\(^3\).g\(^{-1}\).s\(^{-1}\)). Rate constants are calculated for a Maxwell distribution function as follows:

\[ \langle \sigma_{th} \cdot v_r \rangle = \int_{0}^{\infty} \sigma_{th} \cdot f(v_r) \, dv_r. \tag{3} \]

As in [3], the cross section for charge transfer collisions could also be obtained experimentally using the expression:

\[ \sigma_{exp} = \frac{kT_g \cdot \frac{d}{dp}}{\nu} \int_{0}^{\infty} \sigma_{th} \cdot f(v_r) \, dv_r, \] \[ \tag{4} \]

where \( \nu \) is the rare gas ions velocity, \( T_g \) is the gas temperature, and \( d(1/\tau)/dp \) is the first derivative of the experimentally obtained dependence \( 1/\tau = f(p) \), where \( p \) is the saturated vapour pressure of the medium investigated and \( \tau \) is the pulse duration (FWHM) of the spontaneous emission from a transition whose upper level is populated via a charge transfer.

If the excitation energy of an atom \( A \) is greater than the ionization energy of a particle \( B \), Penning ionization takes place according to the following scheme \( A^* + B \rightarrow A + B^+ + e^- + \Delta(\infty) \), where \( A^* \) denotes a metastable atom of helium or neon, \( B^+ \) is the excited ion state to which the atom-target is ionized and excited, and \( \Delta(\infty) \) is the infinite separation energy defect \( \Delta(\infty) = E(A^*) - E(B^+) \), which is carried away by the electron emitted. Assuming that the process takes place by electron exchange between metastable and target atom, the cross-sections for Penning ionization into ion ground state are calculated as follows [4]:

\[ \sigma_{PI} \approx \pi R_0^2 \cdot \frac{n_e \cdot e^{-d/E_i}}{\sqrt{E_i \cdot v_r \cdot r_b^2}} \cdot 10^7, \tag{5} \]

where \( R_0 \) is the sum of the hard core radii of \( A^* \) and \( B \) \( (r_A^* + r_B = R_0) \), \( E_i \) is the ionization potential of \( B \) in eV, \( v_r \) is the relative velocity in cm/s, \( n \) is the number of equivalent electrons in the outer shell of \( B \), and \( d \) is the effective wall thickness if \( R = R_0 \). All lengths are in Å. The ionization into excited states of \( B^+ \) is described by expression (9) if the corresponding quantities – \( n_k, E_k^i \) and \( d_k \) for the \( k \)-th state – are substituted. For gas discharges, it is useful to replace \( v_r \) with the gas temperature \( T_g \) in K using the expression \( v_r = \frac{2kT_g}{\mu_r} \), where \( \mu_r \) is the reduced mass of the system and \( k \) is the Boltzmann constant.

In order to obtain the gas temperature distribution in the discharge zone, the following steady-state heat conduction equation is solved considering an uniform power input and assuming that the gas temperature varies only along the radial direction:

\[ \text{div} \left( k \cdot \text{grad} T_g \right) + q_v = 0, \tag{6} \]
where \( k \) is the thermal conductivity, \( T_g \) is the gas temperature, and \( q_v \) is the power deposited into the discharge per unit volume. The dependence of the thermal conductivity \( k \) of helium or neon is given as in [5] by

\[
k = B T_g^a,
\]

where \( B \) and \( a \) are constants specific for each gas. These constants are obtained through fitting the corresponding experimental data taken from [6] for helium and neon, respectively, and the solution of (6) in [5]. For calculation of characteristic constants it is convenient to use the average gas temperature, which is obtained by averaging over the radius [5]:

\[
\langle T_g \rangle = \frac{4 B}{(2 + a)} q_v R^2 \left( T_0^{2 + a} - T_w^{2 + a} \right),
\]

where \( T_0 = T_g(r=0) \).

2. Results and discussion

In table 1 the results, concerning radial gas temperature distribution and diffusion coefficients for rigid sphere and Lenard-Jones models are summarized at the discharge conditions, which are optimal for laser oscillation.

Table 1. Radial gas temperature distribution and the diffusion coefficients for rigid sphere and Lenard-Jones models.

| Binary system | \( T_w \) (K) | \( R \) (mm) | \( q_v \) (W.cm\(^{-3}\)) | \( \mu_r \) (amu) | \( P \) (Torr) | \( d_{12} \) (Å) | \( \sigma_{12} \) (Å) | \( \varepsilon_{012}/k \) (K) | \( D_{12}^{1} \) (cm\(^2\).s\(^{-1}\)) | \( D_{12}^{2} \) (cm\(^2\).s\(^{-1}\)) |
|---------------|--------------|-------------|-----------------|-------------|-------------|--------------|--------------|----------------|-----------------|----------------|
| He-Tl         | 650          | 5           | 10              | 1090        | 3.93        | 10           | 2.86         | 2.99           | 155.0           | 316.0           | 374.0         |
| Ne-Tl         | 650          | 5           | 10              | 1755        | 18.38       | 10           | 3.06         | 3.12           | 277.7           | 259.6           | 313.7         |
| He-I          | 650          | 5           | 10              | 1090        | 3.88        | 10           | 2.45         | 3.51           | 79.6            | 432.0           | 301.5         |
| Ne-I          | 650          | 5           | 10              | 1755        | 17.43       | 10           | 2.65         | 3.65           | 142.5           | 354.3           | 263.4         |

\( T_w \) - optimal tube wall temperature, \( R \) – discharge zone radius, \( q_v \) - average input power per unit volume, \( \langle T_g \rangle \) - average gas temperature, \( p \) – optimal mixture pressure, \( D_{12}^{1} \) and \( D_{12}^{2} \) – diffusion coefficients for the rigid sphere and 12-6 Lenard-Jones models, respectively.

Using the experimental technique described in detail in [8], the dependence \( 1/\tau = f(p) \) is obtained for the Tl\(^+\) laser lines - 247.7, 260.5, 695.0 and 595.0 nm. The saturated vapour pressure of TlI versus the reservoir temperature is obtained through fitting the corresponding experimental data taken from [7]. The first derivative \( d(1/\tau)/dp \) of this dependence is simply the coefficient of the linear part slope of the curve. It is determined for each Tl\(^+\) line and used to obtain the charge transfer cross section using equation (4). Table 2 shows the theoretically and experimentally obtained cross section and rate constant for charge transfer population of some Tl\(^+\) excited states.

Table 2. Theoretically and experimentally obtained cross section and rate constant for charge transfer population of some Tl\(^+\) excited states.

| Impact Couple | \( \lambda \) (nm) | \( \Delta(\alpha) \) (eV) | \( G \) | \( \langle T_g \rangle \) (K) | \( \alpha \) (10\(^{-24}\) cm\(^3\)) | \( \sigma_{th} \) (10\(^{-15}\) cm\(^2\)) | \( <\sigma_{th}.V_r> \) (10\(^{-6}\) cm\(^3\).s\(^{-1}\)) | \( \sigma_{exp} \) (10\(^{-15}\) cm\(^2\)) |
|---------------|-------------------|------------------|-----|-----------------|------------------|-----------------|-----------------|-----------------|
| He\(^-\)-Tl   | 247.7             | 0.076            | 0.397 | 1090            | 10.61            | 7.894            | 1.697            | 8.3             |
| He\(^-\)-Tl   | 260.5             | 0.664            | 0.139 | 1090            | 10.61            | 4.047            | 0.870            | 3.6             |
| Ne\(^-\)-Tl   | 695.0             | 0.275            | 0.540 | 1755            | 10.61            | 6.867            | 0.865            | 7.4             |
| Ne\(^-\)-Tl   | 595.0             | 0.319            | 0.462 | 1755            | 10.61            | 6.583            | 0.829            | 4.4             |

\( \lambda \) - the wavelength of the line whose upper laser level is populated via charge transfer, \( \Delta(\alpha) \) - the infinite separation energy defect, \( G \) - describes the cross section dependence on \( \Delta(\alpha) \), \( \langle T_g \rangle \) - the average gas temperature, \( \alpha \) - the dipole polarizability of the metal atom, \( \sigma_{th} \) - the calculated cross section, \( <\sigma_{th}.V_r> \) - the corresponding rate constant, \( \sigma_{exp} \) - the experimentally obtained cross section.
As can be seen, the discrepancy between the theoretically and experimentally obtained cross sections varies from 5\% to 50\%, with the averaged value being about 15\%. These results, together with those obtained in [8] for the charge transfer population of some Cu\(^+\), Ag\(^+\), and I\(^+\) excited states (average discrepancy about 30\%), show that the method proposed in [8] and in this paper for calculation of the charge transfer cross sections and rate constants, although being semi-classical, yield sufficiently fair agreement with the experiment.

Cross-sections and rate constants for the Penning ionization into Tl\(^+\) and I\(^+\) ground and excited states are also calculated for collisions between the He and Ne metastable atoms and Tl and I target atoms. The results are presented in table 3. On the contrary, the method chosen in this paper is much more useful and affords an opportunity to obtain rate constants for ion level population by Penning ionization, which is of great importance for the kinetic models.

| Collision partners | Ti\(^+\) or I\(^+\) excited state | \(E_i^k\) (eV) | \(\sigma_{PI}\) (10\(^{-14}\) cm\(^2\)) | \(<\sigma_{PI}.v_{r}>\) (10\(^{-10}\) cm\(^3\).s\(^{-1}\)) |
|--------------------|------------------------------------|----------------|-----------------|-----------------|
| He\(^m\) - I | 5p\(^4\) 3P\(_2\) | 10.451 | 8.469*10\(^{-1}\) | 5.546 |
| He\(^m\) - I | 5p\(^4\) 3P\(_0\) | 11.25 | 6.890*10\(^{-1}\) | 4.512 |
| He\(^m\) - I | 5p\(^4\) 3P\(_1\) | 11.33 | 6.752*10\(^{-1}\) | 4.422 |
| He\(^m\) - I | 5p\(^4\) 1D\(_2\) | 12.15 | 5.516*10\(^{-1}\) | 3.612 |
| He\(^m\) - I | 5p\(^4\) 1S\(_0\) | 14.50 | 3.219*10\(^{-1}\) | 2.108 |
| He\(^m\) - I | 6s\(^5\) 3P\(_0\) | 20.50 | 9.900*10\(^{-1}\) | 0.649 |
| He\(^m\) - I | 5p\(^5\) 3P\(_2\) | 20.61 | 9.717*10\(^{-1}\) | 0.634 |
| He\(^m\) - I | Total | - | 32.81 | 21.48 |
| Ne\(^m\) - I | 5p\(^4\) 3P\(_2\) | 10.451 | 14.92*10\(^{-1}\) | 4.609 |
| Ne\(^m\) - I | 5p\(^4\) 3P\(_0\) | 11.25 | 11.99*10\(^{-1}\) | 3.705 |
| Ne\(^m\) - I | 5p\(^4\) 3P\(_1\) | 11.33 | 11.74*10\(^{-1}\) | 3.626 |
| Ne\(^m\) - I | 5p\(^4\) 1D\(_2\) | 12.15 | 9.476*10\(^{-1}\) | 2.927 |
| Ne\(^m\) - I | 5p\(^4\) 1S\(_0\) | 14.50 | 5.355*10\(^{-1}\) | 1.654 |
| Ne\(^m\) - I | Total | - | 53.48 | 16.52 |
| He\(^n\) - Tl | 6s\(^2\) 3S\(_0\) | 6.1083 | 9.544*10\(^{-1}\) | 6.213 |
| He\(^n\) - Tl | 6p\(^3\) 3P\(_0\) | 12.24 | 1.391*10\(^{-1}\) | 0.906 |
| He\(^n\) - Tl | 6p\(^3\) 3P\(_1\) | 12.61 | 1.266*10\(^{-1}\) | 0.824 |
| He\(^n\) - Tl | 6p\(^3\) 3P\(_2\) | 13.76 | 0.948*10\(^{-1}\) | 0.617 |
| He\(^n\) - Tl | 6p\(^1\) 3P\(_0\) | 15.49 | 0.632*10\(^{-1}\) | 0.411 |
| He\(^n\) - Tl | 7s\(^3\) 3S\(_1\) | 19.16 | 0.288*10\(^{-1}\) | 0.188 |
| He\(^n\) - Tl | 7s\(^1\) 3S\(_0\) | 19.50 | 0.269*10\(^{-1}\) | 0.175 |
| He\(^n\) - Tl | 0A\(_2^+\) | 19.80 | 0.254*10\(^{-1}\) | 0.165 |
| He\(^n\) - Tl | 6d\(^1\) 3D\(_2\) | 20.39 | 0.226*10\(^{-1}\) | 0.147 |
| He\(^n\) - Tl | 6d\(^1\) 3D\(_1\) | 20.51 | 0.221*10\(^{-1}\) | 0.144 |
| He\(^n\) - Tl | 6d\(^1\) 3D\(_0\) | 20.55 | 0.219*10\(^{-1}\) | 0.143 |
| He\(^n\) - Tl | 6d\(^1\) 3D\(_3\) | 20.59 | 0.217*10\(^{-1}\) | 0.141 |
| He\(^n\) - Tl | Total | - | 15.48 | 10.07 |
| Ne\(^n\) - Tl | 6s\(^2\) 3S\(_0\) | 6.1083 | 18.30*10\(^{-1}\) | 5.055 |
| Ne\(^n\) - Tl | 6p\(^3\) 3P\(_0\) | 12.24 | 2.407*10\(^{-1}\) | 0.724 |
| Ne\(^n\) - Tl | 6p\(^3\) 3P\(_1\) | 12.61 | 2.180*10\(^{-1}\) | 0.656 |
| Ne\(^n\) - Tl | 6p\(^3\) 3P\(_2\) | 13.76 | 1.607*10\(^{-1}\) | 0.483 |
| Ne\(^n\) - Tl | 6p\(^1\) 3P\(_1\) | 15.49 | 1.046*10\(^{-1}\) | 0.315 |
| Ne\(^n\) - Tl | Total | - | 25.54 | 7.683 |

\(a\) \(E_i^k\) – excited ion state energy, \(\sigma_{PI}\) – calculated Penning ionization cross section, 
\(<\sigma_{PI}.v_{r}>\) - corresponding rate constant.
3. Conclusions
Cross sections and respective rate constants for thermal energy charge transfer reactions into some Tl$^+$ and I$^+$ excited states are theoretically and experimentally obtained for a gas discharge in He-TlI and Ne-TlI mixtures. The correlation between the cross section experimentally and theoretically obtained for the case of He$^+$-Tl and Ne$^+$-Tl impact couples shows that the method applied at first for the charge transfer population of some Cu$^+$, Ag$^+$, and I$^+$ excited states, although semi-classical, yield sufficiently fair agreement with the experiment (averaged discrepancy of about 20 %) and would be very helpful in the prediction and understanding of numerous charge transfer processes in many phenomena.

The diffusion coefficients of thallium and iodine atoms in binary system with helium and neon are calculated on the basis of 12-6 Lenard-Jones and rigid sphere models.

Cross-sections and rate constants for Penning ionization into Tl$^+$ and I$^+$ ground and excited states are calculated for collisions between He and Ne metastable atoms and Tl and I target atoms. The method chosen in this work is preferable in comparison with the widely used formulae based on the rigid sphere radius. It enables us to obtain rate constants for ion level population by Penning ionization, which is of great importance for the kinetic models. Since the characteristic constants studied depend on the gas temperature, the radial gas temperature distribution is also calculated through solving the heat conduction equation.

Acknowledgements
This work was supported by project of Chinese - Bulgarian Scientific and Technological Cooperation 2K-11-02/2006 “Ultraviolet CuBr and infrared SrBr$_2$ lasers”.

References
[1] Reid R C and Sherwood T K 1966 The properties of gases and liquids (New York: McGraw-Hill Book Company)
[2] Turner-Smith A R, Green J M and Webb C E 1973 J. Phys. B: Atom. Molec. Phys. 6 114-30
[3] Aleinikov V C and Ushakov V V 1972 Optika i Spectroskopiya 33 214-21
[4] Hotop H and Niehaus A 1969 Z. Physik. 228 68-88
[5] Astadjov D N, Vuchkov N K and Sabotinov N V 1988 IEEE J. Quantum Electron. 24 1927-35
[6] Handbook 1991 Tables of physical constants ed Grigoryev I S and Meylihov E Z (Moscow: Energoatomizdat) pp 340-4
[7] Handbook 1976 Tables of physical constants, ed Kikoin I K (Moscow: Atomizdat) pp 206-7
[8] Temelkov K A, Vuchkov N K and Sabotinov N V 2007 J. Phys: Conf. Series 63 012017