Penning ionization cross sections and rate constants

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Abstract. Penning collisions determine the creation of population inversion and the output parameters in a number of ion metal vapor lasers. Some different gaseous additives to the buffer gas also improve metal vapor laser operation via Penning impacts. Assuming that the process takes place by electron exchange between metastable and target atom, cross-sections and rate constants for Penning ionization into ion ground state are calculated for the metastable atoms He and Ne, and 22 target metal atoms, which are active particles in the metal vapour lasers. Cross-sections and rate constants for Penning ionization into excited ion states of the copper and bromine atoms are also calculated.

1. Introduction
It is of great importance for metal vapor lasers to obtain a laser oscillation on new metal ion transitions in the vacuum and deep ultraviolet (VUV and DUV) spectral region. That will make this important group of lasers more competitive.

Lately there has been a widespread interest in the ion metal vapor lasers, operating below 300 nm in the deep ultraviolet (UV) spectral region such as Ne-Cu+ (248.6 nm ÷ 274.0 nm), He-Ag+ (224.3 nm and 227.7 nm) and He-Au+ (226.4 nm ÷ 295.9 nm) lasers. An UV Cu+ laser oscillation at four Cu+ lines - 248.6, 252.9, 260.0, and 270.3 nm, with the highest average output power (1.3 W at multiline operation and 0.85 W on the 248.6 nm laser line), peak pulse power on the 248.6 nm laser line (3.25 W) and specific average output power at an active volume of 23 cm³ (57 mW/cm³ at multiline operation and 37 mW/cm³ on the 248.6 nm laser line) in a Ne-CuBr nanosecond pulsed longitudinal discharge was obtained [1,2]. The UV laser radiation was also characterized with high beam quality (beam divergence lower than 100 µrad) and narrow linewidth (about 0.3 pm). These results opened new prospects for the UV Cu+ laser utilization.

Penning ionization into excited states determines the creation of population inversion and output parameters in a number of ion metal vapor lasers. On the one hand, upper laser levels of several ion metal vapor lasers are populated via Penning collisions. For example, Penning ionization into excited states is a pumping reaction for the He-Cd+ laser operating at 325.0-nm and 441.6-nm lines. On the other hand, Penning collisions are responsible for a population of the lower laser levels and ion metastable levels playing an important role in the creation of inverse population (negative effect - Ne-Cu+ laser). For example, the increase of the Cu+ metastable levels population by Penning collisions
leads to a decrease of the effective probability for spontaneous radiative decay of the lower laser level by radiation trapping and hence to an inversion population decrease. Some different gaseous additives to the buffer gas also improve metal vapor laser operation via Penning collisions. On this base it is assumed that Penning collisions could play an important role in the creation of population inversion on new possible metal ion transitions. That requires obtaining cross sections and rates constants for Penning ionization into ion ground and excited states.

2. Theory

Ionization reactions of excited atoms with other particles at thermal energies play an important role in many phenomena, such as gaseous discharges, shock waves, photolysis, radiolysis, and plasmas in general. If the excitation energy of an atom (A) is greater than the ionization energy of a particle (B), \( E'(A) > IP(B) \), Penning ionization

\[
A^* + B \rightarrow A + B^+ + e^- (Ee_1) + \Delta E
\]

usually is the most important process, in which the emitted electron carries away an energy close to the difference of the excitation energy of (A) and the ionization energy of (B), \( Ee_1 = E'(A) - IP(B) \). If \( \Delta E = Ee_1 - [E'(A) - IP(B)] > E_{kin} \), the relative kinetic energy of the collision, the molecular ion \( AB^+ \) is formed. This process is called associative ionization. Another associative ionization process, in which, however, the emitted electron carries away almost no energy, can occur if \( E'(A) < IP(B) \). This process is called Hornbeck-Molnar process, and is partly responsible for the formation of the rare gas molecular ions, \( A_2^+ \), in gaseous discharges.

The goal of the investigation in [3] has been to obtain data, which may help to clarify the mechanism of Penning ionization processes. Two processes could control the Penning ionization cross section:

\[
\begin{align*}
A^*[1] + B[2] & \rightarrow A[1] + B^+ + e^- [2] \\
A^*[1] + B[2] & \rightarrow A[2] + B^+ + e^- [1]
\end{align*}
\]

where \([1]\) and \([2]\) characterize the two electrons involved, namely the excited electron of the projectile \([1]\) and one of the ground state electrons of the target \([2]\).

In the first process (2) no electron is exchanged. Using the simple "potential curve" picture, each of the systems \( A^* + B \) and \( A + B^+ \) has been assigned a potential curve \( V_1 \) and \( V_2 \), and the actual ionization has been described as the vertical transition \( V_1 \rightarrow V_2 \) between these curves. In this treatment, the exchange process (3) has been neglected and the process has been described as two simultaneous optical transitions, \( A^* \rightarrow A \) and \( B \rightarrow B^+ + e^- \), which limits the application of the derived expression to the case where \( A^* \rightarrow A \) is an allowed transition. In the second process an electron exchange occurs. The process (3) can be viewed as the "tunneling" of the electron \([2]\), initially bound to \( B \) through the potential barrier between \( A \) and \( B \), followed by an Auger emission of electron \([1]\).

This proposed model is in close analogy to the theory of Auger emission of electrons from metal surfaces by metastables. It does not seem to be clear from purely theoretical arguments whether process (2) or (3) predominates. It has been shown in [3] that there is, however, some experimental evidence for the case that \( A^* \) is a metastable atom, which indicates that the exchange process (3) controls the cross section.

If (3) is the only important process in Penning ionization by metastables, its cross section may be estimated. The cross section \( \sigma_{ex} \) then can be obtained by assuming a "billiard ball" collision of \( A^* \) and \( B \). Thus it has been obtained in [3]:

\[
\sigma_{ex} \approx \pi R_0^2 \cdot \frac{n e^{-d\sqrt{E_i}}}{\sqrt{E_i \cdot v_r \cdot r_b^2}} \cdot 10^7
\]

In expression (4), \( R_0 \) is the radius of the "billiard ball", i.e. 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 electronvolts, \( v_r \) 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 Angströms. The ionization into excited states of \( B^+ \) is described by expression
(4) if the corresponding quantities – \( n_k, E_k \) and \( d_k \) for the k-th state – are inserted. For the gas discharges it is useful to replace \( v_r \) with the gas temperature, \( T_g \) in K, using the expression
\[
v_r = \sqrt{\frac{2k_B T_g}{\mu}},
\]
where \( \mu \) is the reduced mass of the system.

3. Results
In order to explain the abovementioned experimental results obtained with the UV Cu\(^+\) Ne-CuBr laser the mechanism for formation of inverse population on the 248.6-nm transition was considered and a simplified model which describes the kinetic processes in a nanosecond pulsed longitudinal Ne-CuBr discharge afterglow was proposed. Schematic diagram of the energy levels of copper, neon and bromine ions, and neon metastables is shown in figure 1.

![Figure 1. Schematic diagram of energy levels of copper, neon and bromine ions, and neon metastables.](image)

Upper laser level 5s \(^3\)D\(_1\), lying directly below Ne ion ground state, is populated via charge exchange reaction. The lower laser level 4p \(^3\)F\(_2\) is mainly depopulated by UV spontaneous emission to the Cu\(^+\) 4s \(^3\)D\(_{1,2,3}\) metastable levels. The lower laser level and Cu\(^+\) metastable levels are populated via Penning collisions with Ne metastables. The increase of the Cu\(^+\) metastable levels population leads to a decrease of the effective probability for spontaneous radiative decay of the lower laser level by radiation trapping and hence to an inversion population decrease. The cross sections and the respective rate constants for Penning ionization into ground and excited ion states are presented in table 1.

| Final state - state, to which ground state Cu and Br atoms are ionized via Penning collisions with neon metastables; \( E_i \) and \( E_k \) - ionization potential and energy defect between excited and ground ion levels; \( \sigma_P \) - cross section; \( \langle \sigma_0, v_r \rangle \) - rate constant. |
|-----------------|-----------------|-----------------|-----------------|
| Final state     | \( E_i \) or \( E_{i+k} \) (eV) | \( \sigma_P \) \( (10^{-16} \text{ cm}^2) \) | \( \langle \sigma_0, v_r \rangle \) \( (10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}) \) |
| Cu\(^+\) (1S\(_0\)) | 7.724 | 5.9\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 1.952 |
| Cu\(^+\) (4s \(^3\)D\(_1\)) | 10.444 | 3.0\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 0.988 |
| Cu\(^+\) (4s \(^3\)D\(_2\)) | 10.554 | 2.9\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 0.960 |
| Cu\(^+\) (4s \(^3\)D\(_3\)) | 10.704 | 2.8\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 0.934 |
| Cu\(^+\) (4s) Total | - | 8.7\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 3.742 |
| Cu\(^+\) (4p \(^3\)P\(_0\)) | 16.384 | 0.8\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 0.256 |
| Br\(^+\) (1S\(_0\)) | 11.84 | 3.3\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 10.590 |
| Br\(^+\) (1D\(_2\)) | 12.273 | 6.0\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 19.220 |
| Br\(^+\) (1S\(_0\)) | 13.339 | 2.4\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 7.629 |
| Br\(^+\) (1S\(_0\)) | 15.295 | 1.6\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 5.130 |
| Br Total | - | 13.3\( \times \)10\(^{-16}\) \( T_g \)^\(^{-1/2} \) | 42.569 |
As it can be seen the Br atoms presence in the active medium results in an additional decay of the Ne metastables - population of the ground and excited Br⁺ levels via Penning collisions is about ten times more effective process than the lower laser and metastable Cu⁺ levels population. That was verified by our experiments. The output parameters of the UV Cu⁺ Ne-CuBr laser were three orders of magnitude higher than those of the UV Cu⁺ Ne-Cu described in detail in [4] - 1 W compare to 1 mW.

It was also found out that the addition of 0.15 Torr argon leaded to a ten-time increase in the average output power (10 mW) of the UV Cu⁺ Ne-Cu. In [5] it has been proposed that small amounts of argon could possibly improve the output parameters of the UV Cu⁺ Ne-Cu hollow cathode laser via Penning collisions. In [6] it was reported that the addition of small amounts of hydrogen, 0.02-0.04 Torr, leaded to an increase by more than twice of the average output power of the UV Cu⁺ Ne-CuBr laser. Unfortunately, the mechanism, by which hydrogen atoms and/or molecules influence the inverse population in the Ne-CuBr discharge, could not be determined from our experiments presented in [6], and will be object of future studies. Theoretical predictions of the cross section and rate constant for Penning collisions between neon metastables and hydrogen atoms and molecules will be carried out.

Cross-sections and rate constants for the Penning ionization into ion ground state are also calculated for the metastable atoms He and Ne, and target atoms Cu, Li, Be, Na, Mg, Ca, Al, K, Zn, Se, Rb, Sr, Ag, Cd, Cs, Au, Hg, Tl, Pb, Bi, Sn, Ba, Br, Ar, Kr, which are active particles in the metal vapour lasers. The results are presented in table 2 (a) and (b).

| Metastable atom | Target atom | Cross section \(10^{-16} \text{ cm}^2\) | Rate constant \(10^{-10} \text{ cm}^3 \text{ s}^{-1}\) |
|-----------------|-------------|----------------------------------------|----------------------------------------|
| He              | Cu          | 3.4*10^2*Tg \(^{-1/2}\)                | 2.247                                  |
| Ne              | Cu          | 5.9*10^2*Tg \(^{-1/2}\)                | 1.952                                  |
| He              | Li          | 4.2*10^2*Tg \(^{-1/2}\)                | 3.400                                  |
| Ne              | Li          | 5.4*10^2*Tg \(^{-1/2}\)                | 3.069                                  |
| He              | Be          | 5.9*10^2*Tg \(^{-1/2}\)                | 4.545                                  |
| Ne              | Be          | 7.5*10^2*Tg \(^{-1/2}\)                | 3.869                                  |
| He              | Na          | 3.1*10^2*Tg \(^{-1/2}\)                | 2.153                                  |
| Ne              | Na          | 4.9*10^2*Tg \(^{-1/2}\)                | 1.935                                  |
| He              | Mg          | 4.1*10^2*Tg \(^{-1/2}\)                | 2.842                                  |
| Ne              | Mg          | 6.3*10^2*Tg \(^{-1/2}\)                | 2.452                                  |
| He              | Al          | 1.6*10^3*Tg \(^{-1/2}\)                | 10.724                                 |
| Ne              | Al          | 2.5*10^3*Tg \(^{-1/2}\)                | 9.607                                  |
| He              | K           | 3.1*10^2*Tg \(^{-1/2}\)                | 1.569                                  |
| Ne              | K           | 4.1*10^2*Tg \(^{-1/2}\)                | 1.419                                  |
| He              | Ca          | 3.4*10^2*Tg \(^{-1/2}\)                | 2.299                                  |
| Ne              | Ca          | 5.7*10^2*Tg \(^{-1/2}\)                | 2.018                                  |
| He              | Zn          | 3.3*10^2*Tg \(^{-1/2}\)                | 2.206                                  |
| Ne              | Zn          | 5.7*10^2*Tg \(^{-1/2}\)                | 1.856                                  |
| He              | Se          | 6.7*10^2*Tg \(^{-1/2}\)                | 4.414                                  |
| Ne              | Se          | 1.1*10^3*Tg \(^{-1/2}\)                | 3.675                                  |
| He              | Rb          | 2.1*10^2*Tg \(^{-1/2}\)                | 1.410                                  |
| Ne              | Rb          | 4.0*10^2*Tg \(^{-1/2}\)                | 1.276                                  |
| He              | Sr          | 3.3*10^2*Tg \(^{-1/2}\)                | 2.148                                  |
| Ne              | Sr          | 5.9*10^2*Tg \(^{-1/2}\)                | 1.893                                  |
| He              | Ag          | 2.9*10^2*Tg \(^{-1/2}\)                | 1.935                                  |
| Ne              | Ag          | 5.4*10^2*Tg \(^{-1/2}\)                | 1.680                                  |
| He              | Cd          | 2.7*10^2*Tg \(^{-1/2}\)                | 1.765                                  |
| Ne              | Cd          | 4.8*10^2*Tg \(^{-1/2}\)                | 1.487                                  |
Cross-sections and rate constants for Penning ionization into excited ion states of the abovementioned target atoms could be also calculated as it is done for copper and bromine atoms (table 1). It is verified that all known experimental facts are in qualitative agreement with the estimated ones following the proposed mechanism (3). It seems desirable to carry out a more detailed calculation of the Penning cross section due to the electron exchange process.

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### Table 2(b).

| Metastable atom | Target atom | Cross section $(10^{-16} \text{cm}^2)$ | Rate constant $(10^{-10} \text{cm}^3 \cdot \text{s}^{-1})$ |
|-----------------|-------------|---------------------------------------|-----------------------------------------------|
| He              | Cs          | $2.0\times10^2 Tg^{-1/2}$              | 1.313                                         |
| Ne              | Cs          | $3.9\times10^2 Tg^{-1/2}$              | 1.192                                         |
| He              | Au          | $1.4\times10^2 Tg^{-1/2}$              | 0.883                                         |
| Ne              | Au          | $2.5\times10^2 Tg^{-1/2}$              | 0.743                                         |
| He              | Hg          | $1.6\times10^2 Tg^{-1/2}$              | 1.026                                         |
| Ne              | Hg          | $2.8\times10^2 Tg^{-1/2}$              | 0.843                                         |
| He              | Tl          | $4.0\times10^3 Tg^{-1/2}$              | 25.907                                        |
| Ne              | Tl          | $8.2\times10^3 Tg^{-1/2}$              | 24.640                                        |
| He              | Pb          | $7.4\times10^2 Tg^{-1/2}$              | 4.786                                         |
| Ne              | Pb          | $1.4\times10^3 Tg^{-1/2}$              | 4.130                                         |
| He              | Bi          | $8.6\times10^2 Tg^{-1/2}$              | 5.599                                         |
| Ne              | Bi          | $1.6\times10^3 Tg^{-1/2}$              | 4.835                                         |
| He              | Sn          | $1.1\times10^3 Tg^{-1/2}$              | 7.315                                         |
| Ne              | Sn          | $2.1\times10^3 Tg^{-1/2}$              | 6.364                                         |
| He              | Ba          | $3.4\times10^3 Tg^{-1/2}$              | 2.254                                         |
| Ne              | Ba          | $6.5\times10^3 Tg^{-1/2}$              | 2.003                                         |
| He              | Ar          | $1.5\times10^3 Tg^{-1/2}$              | 1.047                                         |
| Ne              | Ar          | $2.3\times10^3 Tg^{-1/2}$              | 0.800                                         |
| He              | Kr          | $1.8\times10^3 Tg^{-1/2}$              | 1.156                                         |
| Ne              | Kr          | $2.8\times10^3 Tg^{-1/2}$              | 0.899                                         |