

Model of the Dissociative Recombination of Molecular Ions Based on the Statistical “Phase-Space Theory”

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Abstract: In the paper the statistical “phase-space theory” extended for chemical reactions and for dissociative recombination of polyatomic ions is applied to the indirect and direct dissociative recombination of diatomic ions with electrons. Numerical calculations are made for molecular neon ion. The good agreement is obtained with experimental results.

1. Introduction

The dissociative recombination (DR) of molecular ions is one of the dominant processes in which losses of charged particles occur. Therefore it plays an important role in plasma physics and plasma chemistry. In this paper DR of the diatomic molecular ions is considered. It proceeds in steps through two possible reactions mechanisms [1–3]. In the first step the incident electron penetrates into the A_2^+ ionic target and it is captured giving up its energy either by excitation of an electron in the A_2^+ orbitals or to nuclei for their vibrational motion. In the former case repulsive predissociative state A_2'' arises by electronic

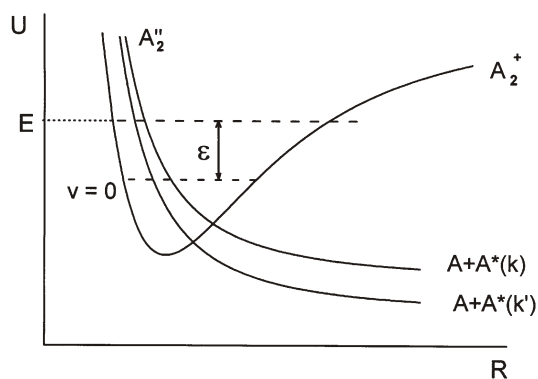


Fig.1. Schematic presentation of potential energy curves for direct dissociative recombination process; – incident electron kinetic energy.

reconfiguration (see Fig. 1). In the latter case vibrationally excited Rydberg intermediate state A_2^R is formed (see Fig. 2).

The repulsive state A_2^+ rapidly decays while the excited state A_2^R has quite a long life-time and only then it turns to a repulsive state. Therefore the former mechanism is called direct DR and the latter is indirect DR. Both direct and indirect DR processes finish with the dissociation of A_2^+ to two atoms A, one of which may be in an excited state $A^*(k)$, $A^*(k')$, where k, k' denote electronic state. We are interested in the rates $k(k)$ [$\text{cm}^{-3} \text{s}^{-1}$] of

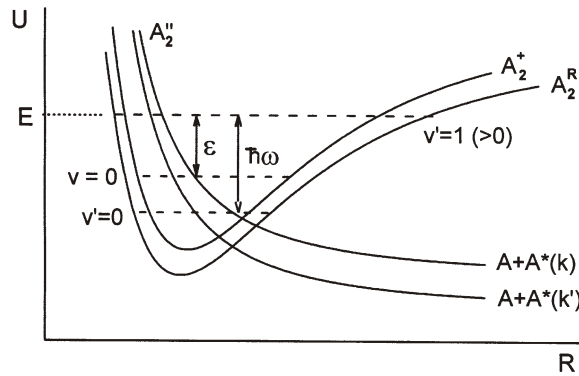


Fig. 2. Schematic presentation of potential energy curves for indirect dissociative recombination process; ϵ – incident electron kinetic energy, v, v' – vibrational states of A_2^+, A_2^R .

occupying various excited states $A^*(k)$. In this paper we will consider only DR running on such conditions that either direct DR or indirect DR is dominant.

Bardsley derived in his configuration interaction theory [1–3] this proportionality between the rate of occupation of the channel $A^*(k)$ through the direct DR and the “temperature T_e ” of incident electrons

$$k(k, T_e) \sim T_e^{-0.5} \quad (1.1)$$

In case of indirect DR he applied the normal resonance theory and using the Breit-Wigner formula he derived temperature variations [2,3] as

$$k(k, T_e) \sim T_e^{-1.5} \quad (1.2)$$

valid if there is only one significant resonant Rydberg state A_2^R . In his treatment A_2^+ in the vibrational ground state was considered.

The most complete set of DR experimental data of all the investigated gases was obtained for the neon. In neon the dissociative channels $\text{Ne}^*(3p_i)$ and $\text{Ne}^*(3d_j)$ are occupied dominantly. Temperature dependences of both the total recombination coefficient $k = k(3p) + k(3d)$ and partial coefficient $k(3d)$, where

$$k(3d) = \sum_{j=1}^{12} k(3d_j),$$

were measured in the afterglow of plasma discharge at $T_e > 1000$ K, when direct DR process dominates, are

$$(T_e) \sim T_e^{0.43} \quad [2,3,8,9] \quad (1.3)$$

$$(3d, T_e) \sim T_e^{0.25} \quad [7] \quad (1.4)$$

At $T_e = 300$ K:

$$(3p) = 0.74, \quad (3d) = 0.26 \quad [9] \quad (1.5)$$

Assuming that

$$(3p, T_e) \sim T_e^{0.5} \quad (1.6)$$

Malinovský and Lukáč [10] showed that (1.4) and (1.5) imply (1.3). All the experimental data were obtained at the laboratory gas temperature ~ 300 K.

As we can see, there exists a certain discrepancy between the theory and the experiment since Bardsley proposed the same temperature dependence (1.1) of recombination coefficients for various channels while in reality (3p) and (3d) coefficients show different dependences (1.6) and (1.4). At the same time the coefficient (3d) falls with increasing electron temperature much more slowly than Bardsley proposed. In our model we try to explain this discrepancy.

2. Model Based on the Statistical “Phase-Space Theory”

We start from the indirect DR since the existence of intermediate state simplifies further considerations. Later we extend our model to direct DR, too. We are not interested in absolute values of (3p), (3d) coefficients but we focus on their dependences on electron temperature. Carrying out certain modifications (concerning the expression of l_{max} and the parametrisation; see later) we decided to apply, to the indirect DR of diatomic ions, the statistical “phase-space theory” adopted for chemical reactions by Light [4] and for the DR of polyatomic ions by Herbst [5].

This theory is based on the assumption of the existence of a “strong coupling region” which has the following property: mode of its decomposition (exit channel) is independent on the rise of this region (input channel) except through conservation laws.

Herbst showed [5] the intermediate Rydberg state A_2^R could be considered as the “strong coupling region”. Therefore the recombination coefficient $a(k)$ can be expressed from the equation

$$a(k) = \sqrt{\frac{2}{m_i}} \sigma(i) P(i \rightarrow k) \quad (2.1)$$

where $\sigma(i)$ is the cross section of the formation the state A_2^R by electron capture and $P(i \rightarrow k)$ is the probability of its dissociation through the channel k . Kinetic energy and mass of the incident electron are denoted by e and m_e , respectively.

Utilizing the property of "strong coupling region" and the principle of detailed balancing we can express the probability $P(i \rightarrow k)$ as a function of cross sections $\sigma(k \rightarrow i)$ of opposite processes (see [4]). Considering that atoms are sufficiently massive particles the cross section $\sigma(k \rightarrow i)$ for coupling two atoms can be expressed using the semiclassical approximation: the atoms will couple if passing into an impenetrable region with the diameter R_0 . We must separately express the coupling cross section for every total angular momentum J . Due to these facts expressing $\sigma(k \rightarrow i)$ by the method of partial waves as a sum of partial cross sections σ_l we get a sum running only over those orbital angular quantum numbers l of atomic rotation which satisfy the following two considerations:

a) $l < l_{\max}(E, k)$; l_{\max} satisfies

$$\frac{\hbar l_{\max}(l_{\max} + 1)}{2 \mu_k} = R_0^2 [E - V_k(R_0)] \quad (2.2a)$$

where E , V_k and μ_k denote the total energy, the potential curve for the channel k and the reduced mass of two atoms, respectively. Condition a) follows from the energy conservation law.

b) $|l - M_k| \leq J \leq |l + M_k|$, hence $|J - M_k| \leq l \leq |J + M_k|$, (2.2b)

where M_k is the quantum number of the sum of rotational angular momenta of two separate atoms A and A*(k). Condition b) follows from the momentum conservation law.

After several derivations (see [4]) utilizing (2.1) the relation can be obtained

$$\sigma(k) \sim \sqrt{\frac{n(k, J, E)}{n(k, J, E)}} \sim \frac{1}{\sqrt{n(k, J, E)}} \quad (2.3)$$

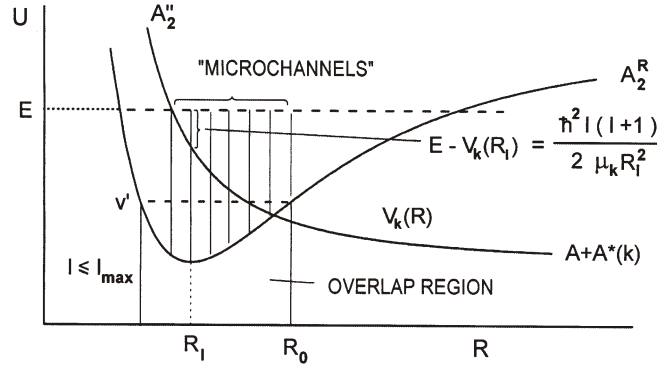


Fig. 3. Schematically presented potential energy curves for recombination process through the channel k with several "microchannels" l . The distance $R_0 = R_{l_{\max}}$.

Where $n(k, J, E) = \sum_l n_l$, summation runs over l satisfying conditions a) and b) for the channel k .

Summation \sum_k runs over all channels, and $E = E_0 + E_{\text{ion}}$, where E_0 is the initial ionic energy.

Factor $n(k, J, E)$ means physically the number of “microchannels” opened in channel k at given J, E (see Fig. 3). Relation (2.3) shows that $\sigma(k)$ is proportional to that portion of all the opened microchannels which belong to the channel k .

With increasing energy of the incident electron the factor $n(k, J, E) = n(k, J, E + E_0)$ (where E_0 is the initial ionic energy) initially rises according to (2.2a) but after the condition (2.2b) becomes stronger than (2.2a), this rising will stop. For this reason in a certain energy interval the coefficient $\sigma(k)$ of the channel k with potential curve lying above the potential curve of the channel k decreases with increasing energy more slowly than $\sigma(k)$. That is why (3d) and (3p) may show different dependences on T_e .

Averaging over the rotational (J) and vibrational (v) states of A_2^+ and over energies of incident electrons gives

$$\sigma(k) \sim \frac{1}{\sqrt{T_e}} \int_{J,v} (2J+1) e^{-\frac{J(J+1)B}{kT_i}} e^{-\frac{h(v+1/2)}{kT_i}} \int_0^\infty \frac{n(k, J, E + E_0)}{n(k, J, E_0)} e^{-\frac{E}{kT_e}} dE \frac{1}{kT_e} \quad (2.4)$$

where B and \bar{E} are ionic characteristics.

3. Extension of the Model to the Direct Recombination

Due to the property of “strong coupling region” the cross section of an electron capture in the indirect DR does not depend on the number of all the opened microchannels. This is in contradiction to the direct DR where the mentioned cross section increases with increasing number of convenient electron reconfigurations inducible by the incident electron. To extend our model to the direct DR we made the following presumption:

We put the cross section $\sigma(k)$ proportional to the number of all the opened microchannels. Then formulae (2.3) and (2.4) change to:

$$\sigma(k) \sim \frac{1}{\sqrt{T_e}} n(k, J, E_0) \quad (3.1)$$

after averaging

$$\sigma(k) \sim \frac{1}{\sqrt{T_e}} \int_{J,v} (2J+1) e^{-\frac{J(J+1)B}{kT_i}} e^{-\frac{h(v+1/2)}{kT_i}} \int_0^\infty n(k, J, E + E_0) e^{-\frac{E}{kT_e}} dE \frac{1}{kT_e} \quad (3.2)$$

Now we shall follow the results of the configuration interaction theory to show that our presumption is quite reasonable.

Bardsley derived the cross section $\sigma_k(\cdot)$ of the direct DR through the channel A_2^+ neglecting rotational motion of the nuclei [1,3]. It follows from this derivation that $\sigma_k(\cdot)$ is proportional to the overlap integral $\left| \left\langle \psi_{A_2}(\mathbf{R}) | \psi_k(\mathbf{R}) \right\rangle \right|_{A_2, k}^2$ between nuclear wave function $\psi_{A_2}(\mathbf{R})$ and $\psi_k(\mathbf{R})$. The overlap integral has approximately the same value as would be obtained when replacing $\psi_k(\mathbf{R})$ by conveniently normalized delta function with its peak near the classical turning point R_E . Therefore

$$\sigma_k(\cdot) \sim \frac{1}{V_k(R_c)} \left| \psi_{A_2}(R_c) \right|^2 \quad (3.3)$$

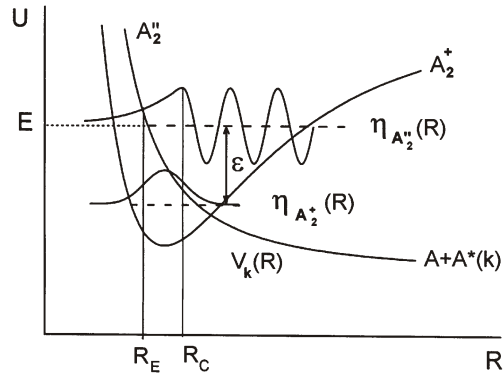


Fig. 4. Schematic presentation of wave functions corresponding to ionic and excited state of molecule A_2 . When R_C is near R_E then $V_k(R_C) - V_{A_2''}(R_C)$.

where $V_k(R) = \frac{d}{dR} V_k(R)$ is the derivative of $V_k(R)$ and the factor $\frac{|V_k(R_C)|^2}{V_k(R_C)}$ is only slightly

dependent on .

Following Bardsley's consideration and taking into consideration also the nuclear rotations we obtain

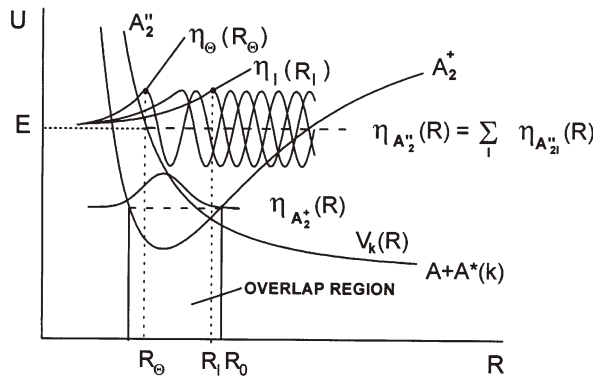


Fig. 5. Schematic representation of potential energy curves and partial waves for different molecular ion or excited molecule.

$$(\) \sim \frac{1}{l} \left| V_k(R_l) A_l (R_l) \right|^2 \quad (3.4)$$

where R_l are the classical turning points of various partial waves (see Fig. 5),

$\frac{\hbar^2 l(l+1)}{2 \mu_k} R_l^2 (E - V_k(R_l))$, the A_l are the amplitudes of partial waves near their turning

points and summation runs over l satisfying the momentum conservation law (condition (2.2b)).

Since $|A_2(R)|$ is significant only in the Franck-Condon region (where $R \approx R_0$), summation can be taken over $l \leq l_{\max}$ (see condition (2.2a)). In the overlap region $v_k(R)$ is almost independent on R . Therefore if we make an approximation putting A_1 equal to the constant and $A_2(R)$ independent on R in the overlap region, then formula (3.4) will turn to (3.1).

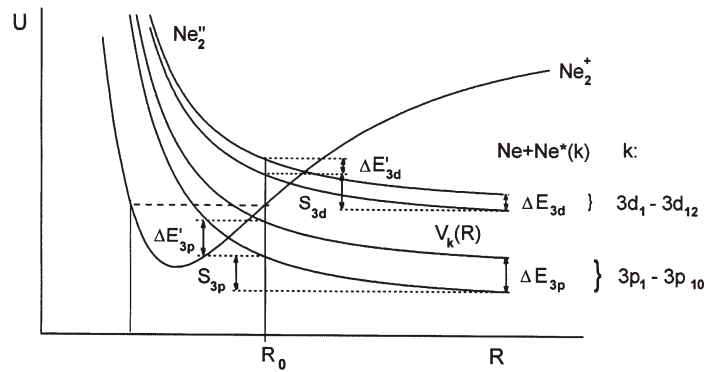


Fig. 6. Schematic representation of potential energy curves and parametrization for the molecular neon (ionic or excited).

4. Numerical Calculations

When computing $n(k, J, + E_0)$ occurring in (3.2) we need to know the course of the potential curve $V_k(R)$ (see Fig. 3). Therefore we need the value $V_k(R_0)$ in (2.2a). These curves have not been computed yet; therefore we shall introduce a certain parameterisation into the model. Meaning of the chosen parameters is obvious from Fig. 6.

We suppose that $W_{3p} = \frac{E_{3p}}{E_{3p}}$ and $W_{3d} = \frac{E_{3d}}{E_{3d}}$. Particular values of the parameters are

chosen so as to correspond with the contemporary known mutual location of the curves and to prove the experimentally measured relation (1.5). Dependences of coefficients $\alpha(3p)$

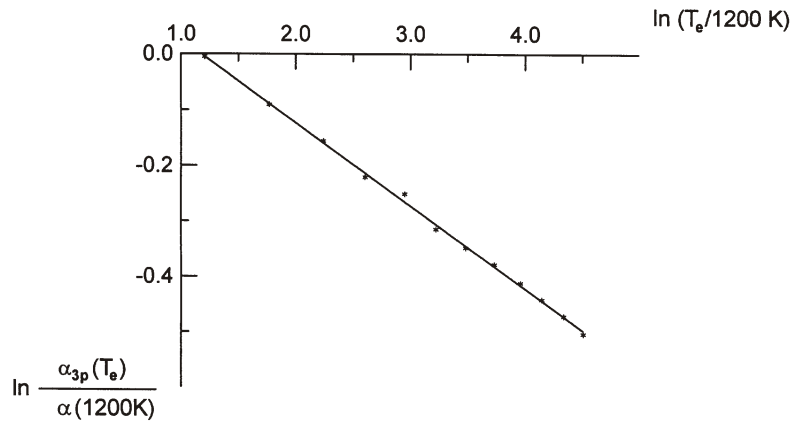


Fig. 7. Calculated relative partial recombination coefficient $\alpha(3p)$ as a function of electron temperature.

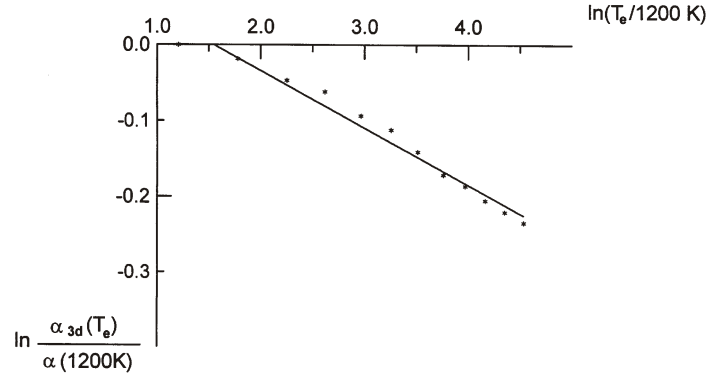


Fig. 8. Calculated relative partial recombination coefficient (3d) as a function of electron temperature.

and (3d) on T_e obtained for parameters $S_{3p} = 1.75$ eV, $W_{3p} = 0.15$, $W_{3d} = 0.55$ and $R_0 = 2 \cdot 10^{-10}$ m are presented in Fig. 7 and Fig. 8. Using the linear regression method we got:

$$\ln(\alpha_{3p}(T_e)) = K1 (0,5 \quad 0,002) \ln T_e,$$

$$\ln(\alpha_{3d}(T_e)) = K2 (0,257 \quad 0,0089) \ln T_e.$$

It is evident that the calculated results are in good agreement with expected dependences (1.4) and (1.6). To summarize our results we need to say that Formula (1.1) has been theoretically predicted just for the case when (k, T_e) can be understood as $(3p, T_e)$, i.e. when (3d) may be neglected. However, the measured values correspond to the dependence $\sim T_e^{-0,43}$. In [10] the authors showed that such dependence can be explained, if total recombination coefficient consists of contributions from 3p and 3d channels and for (3d) the measured dependence $\alpha_{3d} \sim T_e^{-0,25}$ [7] is taken into account. The results calculated from our more general theoretical approach are in good agreement with the dependences (1.4) and (1.6) for the particular channels. They give theoretical explanation of the measured dependence (1.4) hence they support explanation given in [10].

5. Conclusion

Although the presumption introduced in Chapter 3 and the approximations leading to this presumption are open to question and further survey, our model outlines the influence of the nuclear rotation on the dependence of partial recombination coefficients on electron temperature which, as it is shown in Chapter 1, cannot be reliably explained by the previous studies.

Acknowledgement

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