KINETIK THEORY OF PLASMACHEMICAL REACTIONS OF VIBRATIONALLY EXCITED MOLECULES

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ABSTRACT

Kinetics and energy balance for plasmachemical process sti-
mulated by vibrational excitation of the ground electronic
state of reactants are considered. Restrictions are ascer-
tained for ionization degree and specific energy input neces-
sary. The calculations can be applied to CO_2 and H_2O dissoci-
ation, nitric oxides synthesis etc.

1. INTRODUCTION

Vibrational energy of molecules is the most effective one in
surmounting energy barriers for most of endoergic reactions.
This fact combined with high rates of vibrational excitation
and relatively slow VT exchange rates leads to possibility
to create strong difference between vibrational and trans-
lational energies in non-equilibrium gas discharges and to
bring about selectively the required channel of reaction
with extremely high efficiency. The present paper is inten-
ded to study the general features of kinetics and energy
balance in such reactions.

2. POPULATION OF VIBRATIONALLY EXCITED STATES OF MOLECULES IN NON-EQUILIBRIUM PLASMA

Plasma electrons excite commonly lower vibrational levels
while reacting are just highly excited molecules produced
by relaxation processes (mainly VV exchange). Thus, to de-
scribe the kinetics of plasmachemical reactions it is neces-
sary to solve the problem of self-sustained calculation of
vibrational populations and reaction rates taking into con-
sideration VV, VT, eV processes simultaneously. For the dis-
tribution function f(E) (E is the vibrational energy) to be
calculated one can utilize the equation of Fokker-Planch
type:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial E}\left(j_{VV} + j_{VT} + j_{eV} - j_R \right) = 0, \tag{1}$$

which describes the diffusion of molecules in vibrational
energy space. j_{VV}, j_{eV}, j_{VT} flows are attributed to VV, eV,
VT processes respectively, and j_R determines the excited
molecules' flowing to chemical reactions:

$$j_R = \int_E^\infty d\varepsilon \cdot k_R(\varepsilon) \cdot n_o \cdot f(\varepsilon) = J_o - \int_0^E d\varepsilon \cdot k_R(\varepsilon) \cdot n_o \cdot f(\varepsilon).$$

On transforming the collisional term of kinetic equation one can express the relaxation flows in the form 1, 2 :

$$j_{vv} = -D_{vv}(E)\left(\frac{\partial f}{\partial E} + \beta_v f - 2\beta_o x_e \frac{E}{\hbar\omega} f\right) - D_{vv}^{(o)}\frac{\partial}{\partial E}\left[E^2 f^2\left(2x_e\beta_o - \hbar\omega \cdot \frac{\partial^2 \ln f}{\partial E^2}\right)\right],$$

(3)

$$j_{vT} = -D_{vT}(E)\cdot\left(\frac{\partial f}{\partial E} + \tilde{\beta}_o f\right),$$

(4)

$$j_{ev} = -D_{ev}(E)\cdot\left(\frac{\partial f}{\partial E} + \beta_e f\right),$$

(5)

where $D_{vv}(E) = k_{vv}^{(o)}\cdot\exp(-\delta_{vv}\cdot E)\cdot n_o(\hbar\omega)^2$; $D_{vv}^{(o)} = 3 k_{vv}^{(o)} n_o(\hbar\omega)^2 \cdot (\delta_{vv}\hbar\omega)^{-3}$; $D_{vT}(E) = k_{vT}\cdot n_o(\hbar\omega)^2$; $D_{ev}(E) = k_{ev}\cdot n_e(\hbar\omega)^2$; $\beta_v = 1/T_v$; $\beta_e = 1/T_e$; $\tilde{\beta}_o = [1 - \exp(-\hbar\omega/T_o)]/\hbar\omega$; $x_e, \hbar\omega$

- are the unharmonicity constant and vibrational quantum respectively; n_e, n_0 - are the concentrations of electrons and molecules; T_0, T_v, T_e - are translational, vibrational and electron temperature respectively; δ_{vv} - is the characteristic scale for VV relaxation rate changing; k_{vv}^o, k_{ev}, k_{vT}, $k_R(E)$ - are rate constants of VV, VT exchange, vibrational excitation and chemical reaction respectively. It is essential that in deriving (3) – (5) the conditions $E \gg \hbar\omega$, T_e, $T_v > \hbar\omega$, $2\beta_o x_e E < 1$, $\hbar\omega\left|\frac{\partial \ln f}{\partial E}\right| < 1$ were used.

As one can see from (3) – (5), all the relaxation flows except for VV, are linear ones and can be reduced to zero by Boltzmann distributions $f(E)$. Non-linear expression for VV-flow reduces to zero by substituting Treanor distribution $f_T(E)$. Stationary solution of equation (1) would differ from $f_T(E)$ only if the additional consideration of relaxation process differing from VV exchange takes place. For example, in linear approximation simultaneously taking into account VV and VT processes only, distribution function is:

$$f(E) = B\cdot\exp\left\{-\beta_v E + \beta_o x_e \frac{E^2}{\hbar\omega} - \frac{\tilde{\beta}_o - \beta_v}{2\delta_{vv}}\ln\left[1 + \xi(E)\right]\right\},$$

(6)

where B is the normalization constant, $\xi(E) \equiv k_{vT}(E)/k_{vv}(E)$. Substitution of (6) into non-linear part of VV-flow (2) makes it possible to determine the vibrational energy $\tilde{E}$ and the value of $\xi(\tilde{E})$ for which the non-linear part of VV flow breaks its Treanor's character:

$$\xi(\tilde{E}) = \frac{x_e \beta_o}{\delta_{vv}} < 1.$$

(7)

If for the energy $\tilde{E}$ non-linear part preponderates over the linear one

$$f(\tilde{E})\tilde{E} > \frac{D_{vv}(\tilde{E})}{2 D_{vv}^{(o)}}(\delta_{vv}\hbar\omega)^{-1}$$

(8)

then in the vicinity of $\tilde{E}$ the transition of $f(E)$ to plateau will exist.

The previous analysis was dealing with diatomic molecules; however, it is simply generalized for the case of polyatomic molecules in the approximation of selective excitation as well as for full intramolecular equilibrium between the modes [3].

3. VIBRATIONAL RELAXATION AND CHEMICAL REACTIONS FOR NON-EQUILIBRIUM VIBRATIONAL LEVELS' POPULATION

The equation for the first momentum of distribution function enables to express the rate of VT-relaxation of mean vibrational energy in such form:

$$\frac{d\langle\varepsilon\rangle}{dt}\bigg|_{VT} = D_{VT}^{(0)}\cdot f(0) - \int_0^\infty d\varepsilon\cdot f(\varepsilon)\cdot D_{VT}^{(0)}\cdot e^{-\delta_{VV}\varepsilon}\left[\frac{(\tilde{\beta}_o-\hbar\omega)\varepsilon-1}{\hbar\omega}-(\tilde{\beta}_o-\delta_{VV})\right],\quad (9)$$

where $D_{VT}^{(0)} = k_{VT}^{(0)}\cdot n_o\cdot(\hbar\omega)^2 = D_{VT}(E=\hbar\omega)$. Depending on the relation between parameters, the main contribution to integral (9) and, conseqently, to relaxation rate, can be attributed to regions of small or large energies E. In the first case for $T_0 << \hbar\omega$, $\delta_{VV}\hbar\omega << 1$ and for weak influence of Treanor unharmonic correction one can obtain:

$$\frac{d\langle\varepsilon\rangle}{dt}\bigg|_{VT}^{(1)} \simeq k_{VT}^{(0)}\cdot n_o\cdot\frac{\beta_v}{(\beta_v-\delta_{VV})^2},\quad (10)$$

which is in agreement with Losev's formula [4].
It's easy to evaluate the relaxation rate attributed to upper levels for the case of reaction (rate constant k_R) limited by VV-flow to the point E_a:

$$\frac{d\langle\varepsilon\rangle}{dt}\bigg|_{VT}^{(2)} \simeq k_R n_o\hbar\omega\cdot\frac{k_{VT}(E_a)}{k_{VV}(E_a)}\cdot|1-\delta_{VV}\Delta|,\quad (11)$$

where Δ is the characteristic parameter of growing of underintegral expression in (9) in the vicinity of E_a. For highly efficient reactions whose rate constant is $k_R \simeq k_{ev} n_e\hbar\omega/n_o\cdot\Delta Q$ the criterium for VT-relaxation to be attributed mainly to lower levels, is:

$$\frac{k_{ev}}{k_{VV}^{(0)}}\cdot\frac{n_e}{n_o}\cdot\frac{\hbar\omega}{E_a}\cdot\exp(2\delta_{VV}E_a)\cdot|1-2\delta_{VV}\Delta| << 1,\quad (12)$$

where ΔQ is the energy expense for single chemical act. In the reverse case which is realized for sufficiently high ionization degrees, the relaxation is due mainly to upper levels and energy losses to gas heating for each chemical act are:

$$\Delta\varepsilon_{VT} = \hbar\omega\cdot\frac{k_{VT}(E_a)}{k_{VV}(E_a')}\cdot|1-2\delta_{VV}\Delta|.\quad (13)$$

These losses are commonly less then those due to unharmonicity of VV-exchange:

$$\Delta\varepsilon_{VV} = \frac{x_e}{\hbar\omega}\left(E_a^2+\frac{T_v}{\chi}\right),\quad (14)$$

where χ is the conversion degree. Thus, the relaxation rate is determined by (13)-(14) in terms reaction rate which can be obtained analytically for the linear VV – exchange as well as for non-linear one. In the first case rapid diffusion

$D_{vv}(E_a) \gg k_R(E_a)$, we obtain:

$$W_R = n_o \cdot \int\limits_{E_a} d\varepsilon \cdot n_o \cdot f^{(o)}(\varepsilon) \cdot k_R(\varepsilon), \qquad (15)$$

where $f^o(\varepsilon)$ is the distribution function (for example, (6)), taking into account the relaxation processes only. For the reverse case of rapid reaction breaking the distribution function down in the vicinity of E_a :

$$f(E) = f^{(o)}(E) \left[1 - \int\limits_0^\varepsilon d\varepsilon \; \frac{j_R(\varepsilon)}{D_{vv}(\varepsilon) \cdot f^{(o)}(\varepsilon)[1 + \tilde{\xi}(\varepsilon)]} \right], \qquad (16)$$

the reaction rate is expressed as

$$W_R = n_o \cdot \left[\int\limits_0^{E_a} \frac{d\varepsilon}{D_{vv}(\varepsilon) \cdot f^{(o)}(\varepsilon)[1 + \tilde{\xi}(\varepsilon)]} \right]^{-1}. \qquad (17)$$

If the conditions (7)-(8) are fulfilled and non-linear item dominates in VV-flow, then for rapid reaction and $\tilde{E} \leqslant E \leqslant E_a$ f(E) is

$$f(E) \simeq \left[\frac{T_o}{2 \chi_e} \cdot \frac{J_o}{D_{vv}^{(o)}} \left(\frac{E_a}{E^2} - \frac{1}{E} \right) \right]^{1/2}. \qquad (18)$$

In this case the reaction rate is

$$W_R = n_o \cdot J_o \; \frac{D_{vv}^{(o)} \left[f^{(o)}(\tilde{E}) \, \tilde{E} \right]^2}{E_a} \cdot \frac{2 \chi_e}{T_o}. \qquad (19)$$

4. ENERGY BALANCE FOR PLASMACHEMICAL PROCESSES STIMULATED BY VIBRATIONAL EXCITATION OF REACTANTS.

The non-equilibrium plasmachemical reactions rate constants and the rate of vibrational energy transition to heat previously obtained allow to write energy balance equations for the concrete process. As an example let's consider dissociation of CO_2. Since for T_e = 1÷3 eV the main part of electron energy is transmitted to vibrational degrees of freedom of CO_2, then under the conditions of equilibrium between vibrational modes of CO_2, energy balance equations can be written as [3] :

$$\frac{\partial \mathcal{E}_v(T_v)}{\partial t} = k_{ev} \cdot n_e \cdot \hbar \omega_3 \; \theta \left[E_v - k_{ev} \cdot n_e \hbar \omega \cdot t \right] - k_{vT} \cdot n_o \left[\mathcal{E}_v(T_v) - \right. \qquad (20)$$
$$\left. - \mathcal{E}_v(T_o) \right] - k_R(T_v) \cdot n_o \cdot \Delta Q,$$

$$\frac{\partial (C_p T_o)}{\partial t} = k_{vT}(T_o) \cdot n_o \cdot \left[\mathcal{E}_v(T_v) - \mathcal{E}_v(T_o) \right] + d \cdot k_R(T_v) \cdot n_o \cdot \Delta Q, \qquad (21)$$

where E_v - is the energy input to each molecule, $\mathcal{E}_v(T_v)$ - is the vibrational energy of CO_2, ΔQ - is the energy expense for each dissociation act, d - is the relative part of energy transmitted to heat in dissociation act, C_p - is the thermic capacity for the constant pressure; $\hbar \omega_3$ -

- are values of vibrational quanta for deformational and antisymmetric modes. The analysis of equation (20) shows that effective CO_2 dissociation through the vibrational excitation of ground electronic state is brought about when excitation rate exceeds the rate of VT-relaxation. This condition (for $T_V > T_0$) gives a restriction for ionization degree:

$$\frac{n_e}{n_0} \gg \frac{k_{VT}(T_0) \hbar\omega}{k_{ev}(T_e) \cdot \hbar\omega_3} .$$ (22)

Another essential feature of non-equilibrium plasmachemical processes proceeding through vibrational excitation is due to explosive character of VT relaxation. Exponential dependence of k_{VT} on translational temperature leads to the fact that for vibrational temperature [3]

$$T_v^{min.} = E_a / ln\left[\frac{k_{VV}^{(o)}}{k_{VT}(T_0^*) \cdot \Gamma(s)} \cdot \left(\frac{E_q}{T_v^{min}}\right)^{s+1}\right],$$ (23)

corresponding the equality between second and third items in the right-hand part of (20), the reaction through vibrational excitation actually ceases and the residual vibrational energy $\mathcal{E}_v(T_v^{min})$ is expended for unproductive heating of a gas. The value of this threshold energy $E_v^{min} = \mathcal{E}_v(T_v^{min})$ for CO_2, $T_0 \simeq 300°K$ amounts to 0,2 eV and is in good agreement with experimental results [3].

Carrying out plasmachemical processes with high energetic efficiency requires to provide the homogeneity and stationarity of the discharge in chemical reaction zone. Thus it is necessary to determine the increment of thermic instability leading to increase of VT relaxation rate, to superheating of a gas and to breaking of vibrational-translational non-equilibrium. For this reason consider a set of equations for vibrational and translational energies balance, for uninterruption and for conservation of momentum in the case of compressable gas one-dimensional stationary flow:

$$\frac{\partial}{\partial x}(n_0 \cdot v) = 0 \quad , \quad \frac{\partial}{\partial x}(n_0 \cdot v^2 + n_0 \cdot T_0) = 0,$$ (24)

$$\frac{\partial}{\partial x}\left[n_0 \cdot v \cdot \left(c_p T_0 - \frac{v^2}{2}\right)\right] = k_{VT} \cdot n_0^2 \cdot \hbar\omega + d \cdot k_R \cdot n_0^2 \cdot \Delta Q,$$ (25)

$$\frac{\partial}{\partial x}\left[n_0 \cdot v \cdot \mathcal{E}_v(T_v)\right] = k_{ev} \cdot n_e \cdot n_0 \cdot \hbar\omega_3 - k_R n_0^2 \cdot \Delta Q - k_{VT} n_0^2 \hbar\omega,$$ (26)

where v the velocity of a gas. If the condition (22) is fulfilled, then changing of gasdynamic parameters of a flow can be considered as proceeding against the background of rapid establishment of vibrational temperature T_v, and thus only a set of equation (24)-(26) may be analysed. In linear approximation the set (24)-(26) have solutions of such kind:

$$T_0 = T_0(0)\left[1 + \frac{(\nu_{VT} + \nu_R) \cdot (\gamma M^2 - 1)}{2(\nu_{VT} + \nu_R) + \nu_{VT} \hat{k}_{VT}(\gamma M^2 - 1)}\left(exp\left(\frac{\Omega x}{v}\right) - 1\right)\right],$$ (27)

where

$$\Omega = [2(\nu_{VT} + \nu_R) + \nu_{VT} \cdot \hat{\mathcal{R}}_{VT}(\gamma M^2 - 1)] / (M^2 - 1),$$
(28)

$\nu_{VT} = \dfrac{\gamma-1}{\gamma} \cdot \dfrac{K_{VT} \cdot n_0 \cdot \hbar\omega}{T_0}$, $\nu_R = \dfrac{\gamma-1}{\gamma} \cdot \dfrac{\alpha \cdot K_R \cdot n_0 \cdot \Delta Q}{T_0}$ — are the characteristic frequencies for gas heating due to vibrational relaxation and chemical reaction, respectively; $\gamma = C_P / C_V$, $M \equiv \upsilon / \upsilon_3$ — is the Mach number (υ_3 — is the sound velocity); $\hat{\mathcal{R}}_{VT} = \partial \ell n K_{VT} / \partial \ell n T_0$. For the case of flowing with low velocities $M \ll 1$ (and $T_0 \simeq$ 300K, $\nu_{VT} \gg \nu_R$) the characteristic time of instability's evolution is determined by:

$$\Omega^{-1} = [K_{VT} \cdot n_0]^{-1} (3 c_P T_0 / \hbar\omega U_0),$$
(29)

where $U_0 = 72 / T_Q (K)^{1/3}$. The requirement of maintaing the non-equilibrium of a discharge ($T_V > T_0$) in chemical reaction zone leads to more strong restrictions on ionization degree than those of (22). For the supersonic flowing low translational temperature $T_0 \simeq 100K$ leads to significant decrease in the frequency of heating due to vibrational relaxation: $\nu_{VT} \ll \nu_R$. But because of sharp dependence of gasdynamic parameters on the total heat production q associated with chemical reaction, two cases can be distinguished. For $q > q_{cr.}$ the flow parameters are changed appreciably during the time less than that of reaction $\tau_{R}[(\tau_R \Omega) \gg 1]$ and the increment is determined by (26). For $q < q_{cr.}$, i.e., for $\tau_R \Omega \ll 1$ expression (26) can be averaged over heat production in chemical reaction and the increment is determined by:

$$\Omega = \nu_{VT} \cdot [2 + \hat{\mathcal{R}}_{VT}(\gamma M^2 - 1)] / [M^2 1 - \frac{2(\gamma-1)}{\gamma} \alpha \cdot \int \cdot \Delta Q].$$
(30)

The value of $q_{cr.}$ is found from the condition

$$q_{cr.} = T_0 \frac{M^2 - 1}{\frac{\gamma-1}{\gamma}\{[2 + K_{VT}(\gamma M^2 - 1)]\nu_{VT}/\nu_R + 2\}}.$$
(31)

Numerical estimations reveal that bringing about plasmachemical reactions in a supersonic gas flow with $M = 3 \div 5$ for $q < q_{cr.}$ enables to make relaxation length $L = \upsilon / \Omega$ exceed the dimension of a system and to provide high energetic efficiency of a process.

5. REFERENCES

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