

Frequency Dependence of Microwave-assisted Electron-transfer Chemical Reactions

Journal:	<i>Molecular Physics</i>
Manuscript ID	Draft
Manuscript Type:	Full Paper
Date Submitted by the Author:	n/a
Complete List of Authors:	Kouzaev, Guennadi; Norwegian University of Science and Technology, Department of Electronic Systems
Keywords:	electron transfer chemical reactions, classical molecular theory, microwaves

SCHOLARONE™
Manuscripts

Frequency Dependence of Microwave-assisted Electron-transfer Chemical Reactions

Guennadi A. Kouzaev

Department of Electronic Systems, Norwegian University of Science and Technology - NTNU

Trondheim, Norway, E-Mail: guennadi.kouzaev@ntnu.no

Abstract. In this paper, the electron transfer reactions in microwave irradiation field are considered. A theory is developed for these reactions in reactors filled by a mix of reagents and a polar frequency-dispersive and lossy solvent. This mix is described by a system of non-linear differential equations for non-stationary microwave field, heat, liquid dynamics, and chemical molecular kinetics that can be solved in full only numerically. In this paper, a particular solution of this system for the normalized chemical reaction rate coefficient $k = K/A$ with A as the pre-exponent factor is considered for the isothermic reactions for a given temperature T and frequency-temperature dependent complex dielectric permittivity $\tilde{\epsilon}(\omega, T)$ of solvent. It is found that for small normalized free reaction energy $G_0/k_B T \ll 1$, the chemical reactions are supported in a wide frequency band with an increased rate coefficient close to the unit. At higher values of this energy, these reactions are initiated only by heating with a small increase in the frequency bandwidth of reactions. The restrictions of the given theory are considered, and further experimental and semi-classical and quantum-mechanical studies are found important for practical application of these findings.

Keywords: electron transfer chemical reactions, classical molecular theory, microwaves

1. Introduction

Electron-transfer reactions are with the transfer of an electron from one molecule to another through the intermolecular space or along the covalent bridges transforming them into the ion couplings of donor and acceptor molecules. There are several types of these reactions initiated by thermal interactions, infra-red (IR), optical and ultra-violet (UV) irradiation, phonon excitation, and high-frequency oscillation of molecules. The reactions may be initiated in solids, liquids, and gaseous matter. In heterogeneous cases, they occur at the boundary of a solid and liquid. An interesting area of research is the electron-transfer reactions near the nano solid particles, third molecules, catalysts, and in living matter. In many cases and under some conditions, these

reactions are influenced by polar solvers transferring thermal energy to the reactants and influencing the electron's paths in the phase space of chemical reactions [1],[2],[3],[4].

The first theory for electron transfer reactions was given by R.A. Marcus [1],[2],[3], who obtained an Arrhenius-type formula for the rate K of chemical reactions of this type compared well with experimental data under the assumptions that the interacting molecules are in polar liquid which molecules are essentially smaller than molecules of reagents:

$$K = A(T) \exp \left[-\frac{(\lambda + \Delta G_0)^2}{4k_B \lambda T} \right] \quad (1)$$

where $A(T)$ is the pre-exponential factor depending on the type of electron-transfer reactions, molecular stereochemical factor [1],[5],[6]. Other terms in (1): ΔG_0 is the standard free energy of reactions, k_B is the Boltzmann constant, and

$$\lambda = \lambda_0 + \lambda_v \quad (2)$$

is the energy reorganization term consisting of solvation (λ_0) and reactant vibrational (λ_v) components.

The solvation term according to Marcus in SI system of units is

$$\lambda_0 = \left(\frac{\Delta e}{4\pi\epsilon_0} \right)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \cdot \Pi \quad (3)$$

where Δe is the transferred charge measured in C, $a_{1,2}$ are the radii of the reagent molecules represented by spheres, R is the distance between the interacting molecules, ϵ_0 is the vacuum absolute permittivity, and

$$\Pi = \frac{\epsilon_0}{32\pi^2} \left(\frac{1}{\epsilon_\infty^{(r)}} - \frac{1}{\epsilon_s^{(r)}} \right) \quad (4)$$

is the Pekar's factor [7] with $\epsilon_\infty^{(r)}$ and $\epsilon_s^{(r)}$ as the relative permittivities of solver at UV and low frequencies, correspondingly. The first term in the Pekar's formula is associated with the fast electron cloud polarization, and the second one is with the slow rotational motion of dipoles.

The vibrational term λ_v depends on the geometry of interacting molecules, and it should be considered if these modes are involved in the electron transfer reactions [5]. There are many

1
2
3 other modifications of this Marcus formula known considering different effects, including the
4 quantum ones [5].
5
6

7 As seen from formulas (1)-(3), the rate of chemical reactions depends on the environment
8 and can be regulated somehow by choosing the polar solvent properly. Another found properties
9 of electron transfer reactions are their dependence on the frequency of applied heating microwave
10 irradiation. According to the opinions of many authors, this dependence is beyond of thermal
11 effects of microwaves [8],[9],[10],[11].
12
13
14
15

16 In this paper, based on the theory of Marcus, a hypothesis is proposed on the possible nature
17 of the non-thermal microwave effect in electron transfer reactions, and the results of some
18 simulations are given confirming the mentioned idea.
19
20
21
22
23

24 **2. Frequency dependence of electron transfer reaction in the microwave field**

25 Consider the applications of microwaves to a mix of reagents in a polar solvent and study the
26 influence of irradiation on the chemical rate coefficient (1). An analysis of Marcus' formulas and
27 experimental results around these reactions, particularly show that the environmental influence is
28 registered if the solvation term λ_0 is comparable or larger than the vibrational one λ_v . Suppose
29 that energy of microwave quanta is below the thermal one of molecules ($\hbar\omega < k_B T$) with h as the
30 normalized Planck's constant and ω is the cycling frequency of microwaves. Besides, this energy
31 is not enough to transfer electrons directly on higher levels of energy diagram of molecules and
32 this energy to molecules are transferred by friction between rotating molecules. The polar
33 solvation liquid is described classically, and the complex dielectric permittivity can be used for its
34 description.
35
36
37
38
39
40
41
42
43
44

45 According to contemporary knowledge, the permittivity dispersion at low frequencies is
46 with the relaxation processes in dielectrics when the energy of the alternating electric field is spent
47 on heating of liquids or solids through the friction mechanism. For linear lossy dielectrics in the
48 microwave field, instead of static permittivity ϵ_s , the complex one is used [12]. A general formula
49 for the complex permittivity $\tilde{\epsilon}$ of a liquid polar dielectric [12],[13] is:
50
51
52
53
54
55
56
57
58
59
60

$$\tilde{\varepsilon} = \varepsilon_0 \left(\varepsilon_\infty^{(r)} + \frac{\varepsilon_\infty^{(r)} - \varepsilon_1^{(r)}}{1 + j\omega\tau_1} + \frac{\varepsilon_1^{(r)} - \varepsilon_2^{(r)}}{1 + j\omega\tau_2} + \dots + \frac{\varepsilon_{i-1}^{(r)} - \varepsilon_i^{(r)}}{1 + j\omega\tau_i} + \dots + \frac{\varepsilon_{N-1}^{(r)} - \varepsilon_N^{(r)}}{1 + j\omega\tau_N} \right) \quad (5)$$

where τ_i is the i -th relaxation time, $j = \sqrt{-1}$, and $\varepsilon_i^{(r)}$ is a relative permittivity at a frequency well above $2\pi/\tau_i$. In general, the frequency dependence of these parameters is not monotonic and can show extremums. Usually, the parameters in this formula are obtained from measurements and using fittings techniques [13], and, in some cases, only the first two terms can be enough to model even non-Debye liquids ($N > 1$) for low-frequency calculations with the acceptable accuracy. In general, the parameters of (5) are the temperature-dependent, and they can be estimated from molecular theories of dielectrics or measurements.

The imaginary part of (5) defines the temperature of polar liquids and reagents, and it increases liquid temperature T and the pre-exponential factor A but not the free energy of a reaction ΔG_0 in (1). To evaluate the influence of the dispersion of polar liquids, come back to [7] on an electronic theory of crystals where it is shown that in the case of a harmonic electromagnetic (EM) wave the Pekar's coefficient is frequency-dependent:

$$\Pi(\omega) = \frac{\varepsilon_0}{32\pi^2} \left(\frac{1}{\varepsilon_\infty^{(r)}} - \frac{1}{\varepsilon'(\omega)} \right). \quad (6)$$

where $\varepsilon'(\omega) = \text{Re}(\tilde{\varepsilon}(\omega)/\varepsilon_0)$.

Thus, this Pekar's coefficient can be used to evaluate the frequency-dependent electron-transfer reaction using (1) obtained for the static case, and this dependency can be exponentially strong enough if $\lambda_0 \gg \lambda_v$. Additionally, let's notice that the time-dependent thermally-driven electron transfer reactions in dispersive and lossy solvents have been theorized earlier in [14],[15],[16], but the microwave-assisted reactions have been left out of attention yet according to the best knowledge of the Author.

3. Simulation algorithm for the electron transfer reaction rate in microwave reactors

The microwave-assisted chemistry is performed in a vessel inserted into microwave ovens [17],[18],[19], or these vessels can be the ovens themselves [20],[21],[22]. Then, the shape of these vessels influences the EM field and temperature distribution, liquids dynamics, and the point-defined chemical reaction rate. In general, it represents a complicated system of coupled differential linear and non-linear equations solved using powerful computers or supercomputers. Simplification of these systems using the analytical or semi-analytical means similar (1) can be essentially helpful. Consider the formulation of the mentioned system of equations to calculate the rate coefficient (1).

For simplicity suppose that concentration of reagents and the final product is not strong and does not influence the complex permittivity $\tilde{\epsilon}$ of liquids during a chemical reaction. Application of microwaves leads to heating of this liquid with its linear response towards the EM irradiation.

The set of the time-dependent Maxwell equations for this case is

$$\begin{aligned}\nabla \times \mathbf{H}(\mathbf{r}, t) &= \epsilon_0 \frac{\partial (\epsilon^{(r)}(\mathbf{r}, t) \mathbf{E}(\mathbf{r}, t))}{\partial t} + \sigma(\mathbf{r}, t) \mathbf{E}(\mathbf{r}, t), \\ \nabla \times \mathbf{E}(\mathbf{r}, t) &= -\mu_0 \mu^{(r)} \frac{\partial \mathbf{H}(\mathbf{r}, t)}{\partial t}, \\ \nabla \cdot (\epsilon^{(r)}(\mathbf{r}, t) \mathbf{E}(\mathbf{r}, t)) &= \frac{\rho_e(\mathbf{r}, t)}{\epsilon_0}, \\ \nabla \cdot \mathbf{H}(\mathbf{r}, t) &= 0\end{aligned}\tag{7}$$

where \mathbf{E} and \mathbf{H} are the electric and magnetic field intensities, respectively; ϵ_0 and μ_0 are, correspondingly, the vacuum absolute permittivity and permeability with $\epsilon^{(r)}$ and $\mu^{(r)} = const$ are their relative counterparts; σ is the electric conductivity of the medium, ρ_e is the electric charge density, t is time, \mathbf{r} is the coordinate radius-vector, and $\nabla \equiv \mathbf{x}_0 \frac{\partial}{\partial x} + \mathbf{y}_0 \frac{\partial}{\partial y} + \mathbf{z}_0 \frac{\partial}{\partial z}$ is a vector-differential operator.

In problems associated with the heating of lossy dielectric materials or with the MW-assisted chemistry, the material parameters $\left(\varepsilon^{(r)}\right)$ change their values in time slowly in comparison with the period of applied MW field of the cyclic frequency ω . Then, (7) can be used in their complex notation form (8) with j as the imaginary unit and where the slowly varying in time τ field vectors and dielectric parameters are used as independent on fast time t :

$$\begin{aligned}\nabla \times \mathbf{H}(\mathbf{r}, \tau) &= j\omega\varepsilon_0\tilde{\varepsilon}^{(r)}(\mathbf{r}, \tau)\mathbf{E}(\mathbf{r}, \tau), \\ \nabla \times \mathbf{E}(\mathbf{r}, \tau) &= -j\omega\mu_0\mu^{(r)}\mathbf{H}(\mathbf{r}, \tau), \\ \nabla \cdot \left(\varepsilon^{(r)}(\mathbf{r}, \tau)\mathbf{E}(\mathbf{r}, \tau)\right) &= \frac{\rho_e(\mathbf{r}, \tau)}{\varepsilon_0}, \\ \nabla \cdot \mathbf{H}(\mathbf{r}, \tau) &= 0.\end{aligned}\tag{8}$$

The EM equs. (7) and (8) should be supplemented with the heat-transfer and fluid-flow relationships. The heat-transfer equation, which incorporates the convective and conductive heat transfer terms and reflects the conservation of energy, is

$$\rho c_p \left(\frac{\partial T}{\partial \tau} + \mathbf{v} \cdot \nabla T \right) = \nabla \cdot (\kappa \nabla T) + p_d\tag{9}$$

where ρ is the mass density of the heated liquid, c_p is its heat capacity, \mathbf{v} is the flow velocity vector, κ is the thermal conductivity of the material, and p_d is the absorbed in dielectric power density, which quadratically depends on the electric field \mathbf{E} .

The fluid-flow relationships consist of the continuity equation, which expresses the conservation of mass:

$$\frac{\partial \rho}{\partial \tau} + \nabla \cdot (\rho \mathbf{v}) = 0,\tag{10}$$

and the Navier-Stokes equations with the external gravitational force:

$$\rho \left(\frac{\partial \mathbf{v}}{\partial \tau} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla P + \nabla \cdot \mathbf{T} + \rho \mathbf{g}\tag{11}$$

where P is the pressure, \mathbf{g} is the Earth gravitational acceleration, and $\nabla \cdot \mathbf{T}$ is the divergence of the stress deviator tensor, which is equal to $\eta \nabla^2 \mathbf{v}$ for incompressible flow with constant viscosity

$$\eta \text{ where } \nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

The solution of these equations (7)-(11) with properly formulated boundary and initial conditions allows to calculate the temperature and frequency-dependent rate coefficient of electron transfer reactions:

$$K = A(T, \omega) \exp \left[-\frac{(\lambda(T, \omega) + \Delta G_0)^2}{4k_B \lambda(T, \omega) T} \right]. \quad (12)$$

It allows us to calculate once more the complex permittivity of liquid mix varying with temperature.

It is seen the complexity of this multi-physical problem (8)-(12), in spite of employing the analytical expression (12) for the rate coefficient K . Usually, these equations are solved, taking an iteration algorithm with multiple steps in the solutions of them [20]. Another technique is the use of “analytical shapes” of vessels allowing rather simple expressions for EM and other fields [20],[21]. An essential simplification of calculations is available for the micro-sized vessels providing homogeneous distributions of temperature fields inside reactors, etc. Otherwise, only numerical tools are advised to simulation.

4. Estimation of frequency and temperature dependence of the electron transfer rate coefficient

In general, the analytical treatments, in spite their limitations in accuracy and applicability (see, for instance [1],[2],[3] with analysis for (1)), allow obtaining the estimations in a very simple form before full treatments. An example of these estimations is shown below.

The argument of exponent in (12) is evaluated supposing the isothermal condition for the electron transfer reactions and the solved equations (8)-(11) regarding temperature T . For convenience, let's transform this argument in the following way:

$$\frac{(\lambda + \Delta G_0)^2}{4k_B \lambda T} = \frac{1}{\lambda} \left(\frac{\lambda^2}{4k_B T} + \frac{\lambda}{2} \left(\frac{\Delta G_0}{k_B T} \right) + \frac{k_B T}{4} \left(\frac{\Delta G_0}{k_B T} \right)^2 \right). \quad (13)$$

An analysis of (13) shows that to reach a minimum of it and provide the maximal normalized rate coefficient $k = K/A$, it is necessary to decrease strongly $\Delta G_0/k_B T$:

$$\frac{(\lambda + \Delta G_0)^2}{4k_B \lambda T} \approx \frac{\lambda}{4k_B T}. \quad (14)$$

In this case, the normalized rate coefficient k can have a non-thermal influence of microwave irradiation. Otherwise, k decreases with frequency because $\varepsilon'(\omega) \rightarrow \varepsilon_\infty^{(r)}$.

To illustrate this effect, let's model reactions in polar alcohols methanol and ethanol. Although they are not the Debye liquids, here, these solvers are modeled using only two first terms in (5). Then formulas for real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ parts of complex relative permittivities are:

$$\varepsilon'(\omega, T) \approx \varepsilon_\infty^{(r)}(T) + \frac{\varepsilon_s^{(r)}(T) - \varepsilon_\infty^{(r)}(T)}{1 + \omega^2 \tau^2(T)}. \quad (15)$$

$$\varepsilon''(\omega, T) \approx \frac{(\varepsilon_s^{(r)}(T) - \varepsilon_\infty^{(r)}(T)) \omega \tau(T)}{1 + \omega^2 \tau^2(T)}. \quad (16)$$

The imaginary part $\tilde{\varepsilon}(\omega)$ defines the temperature assisted by microwave irradiation by molecular interaction mechanism.

Initially, consider this reaction in the isothermic conditions at $T = 298$ K for which the measurement data for all parameters in (15) and (16) are found in [23]. Fig. 1 shows the methanol and ethanol relative permittivities $\varepsilon'(\omega) = \frac{1}{\varepsilon_0} \text{Re}(\tilde{\varepsilon})$ with $\tau = 46.8$ ps, $\varepsilon_s^{(r)} = 32.6$, and $\varepsilon_\infty^{(r)} = 5.3$ for methanol, and $\tau = 145.1$ ps, $\varepsilon_s^{(r)}(0) = 23.7$, and $\varepsilon_\infty^{(r)} = 3.9$ for ethanol. All curves in Fig. 1 are obtained ignoring any possible molecular resonances in these liquids.

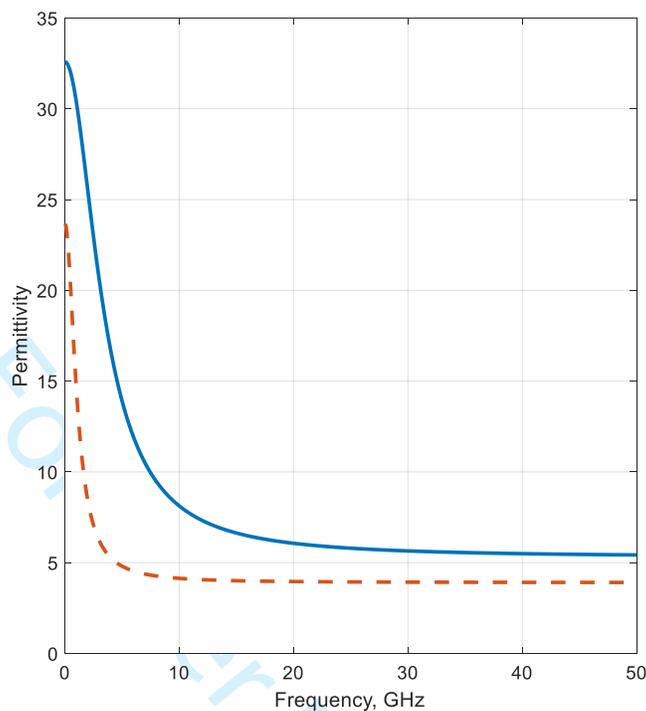


Fig. 1. Frequency dependence of real part of the complex relative permittivity of solvers $\varepsilon'(\omega)$.
Methanol - dash red curve; Ethanol – solid blue curve.

In Fig. 2, the dependencies of the normalized chemical rate coefficients are shown versus frequency given for methanol and ethanol for small $\Delta G_0/k_B T = 0.0005$. It is seen the very large value of the rate coefficient in a wide frequency band with the maximums at certain frequencies.

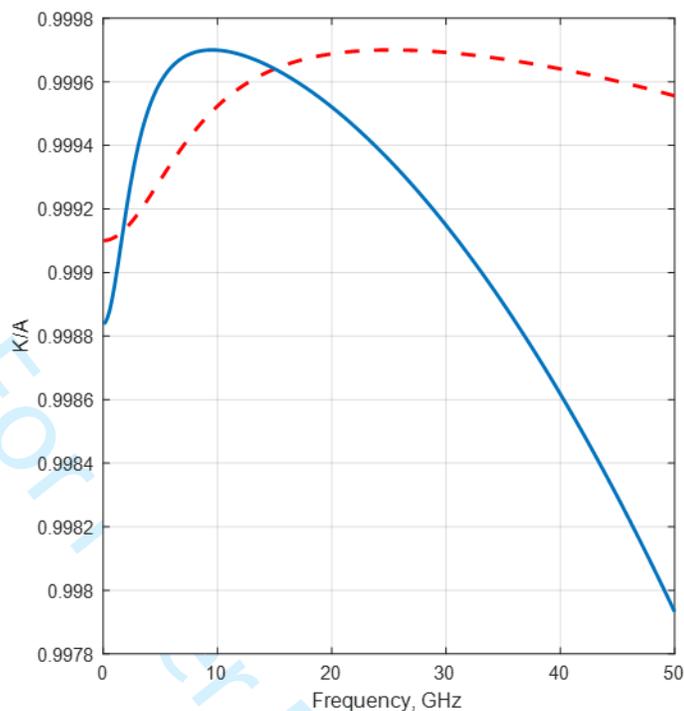


Fig. 2. Normalized Marcus rate coefficient K/A versus frequency for methanol (solid blue curve) and ethanol (dash red curve). $\Delta G_0/k_B T = 0.005$, $a_1 = a_2 = 5 \cdot 10^{-10}$ m, $R = 15 \cdot 10^{-10}$ m, $\Delta e = e = -1.602 \cdot 10^{-19}$ C, and $T = 298$ K.

Unfortunately, increasing $\Delta G_0/k_B T$ leads to an essential fall of the normalized rate coefficient with the decrease of reaction frequency bandwidth (Fig. 3). At large values of $\Delta G_0/k_B T$ the reaction is not supported due to frequency influence out of a very narrow frequency band close to zero frequency. The influence of microwaves is only due to the heating of the liquid.

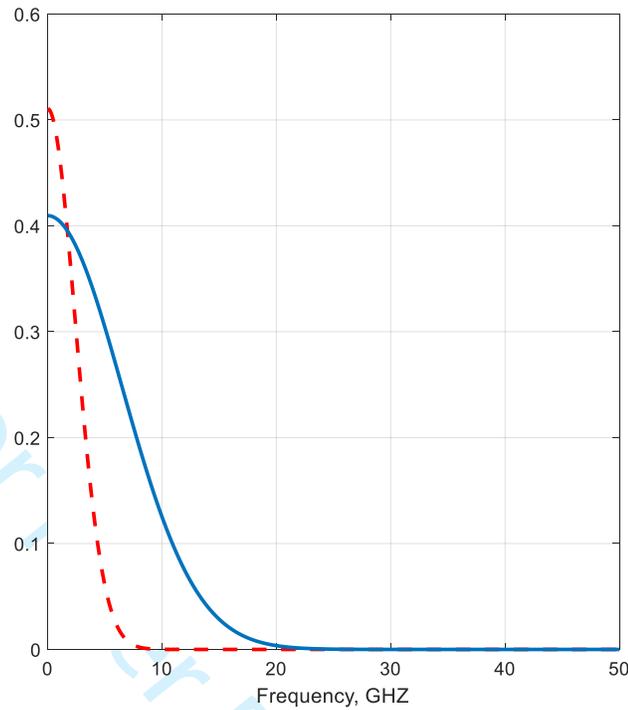


Fig. 3. Normalized Marcus rate coefficient K/A versus frequency for methanol (solid blue curve) and ethanol (dash red curve). $\Delta G_0/k_b T = 0.1$, $a_1 = a_2 = 5 \cdot 10^{-10}$ m, $R = 15 \cdot 10^{-10}$ m, $\Delta e = e = -1.602 \cdot 10^{-19}$ C, and $T = 298$ K.

The influence of temperature is more ambiguous in this case because it leads to an increase in liquid permittivity in certain ranges of temperature [13]. More complicated behavior can show mixes of solvents and non-Debye liquids, which can have multiple extremums of real parts of their permittivities in the frequency and temperature.

Fig. 4 shows the curves given for several values of temperature. Heating causes the increase of the normalized rate coefficient and extension of the frequency bandwidth, although it is not so profound as in the case of decrease of $\Delta G_0/k_B T$.

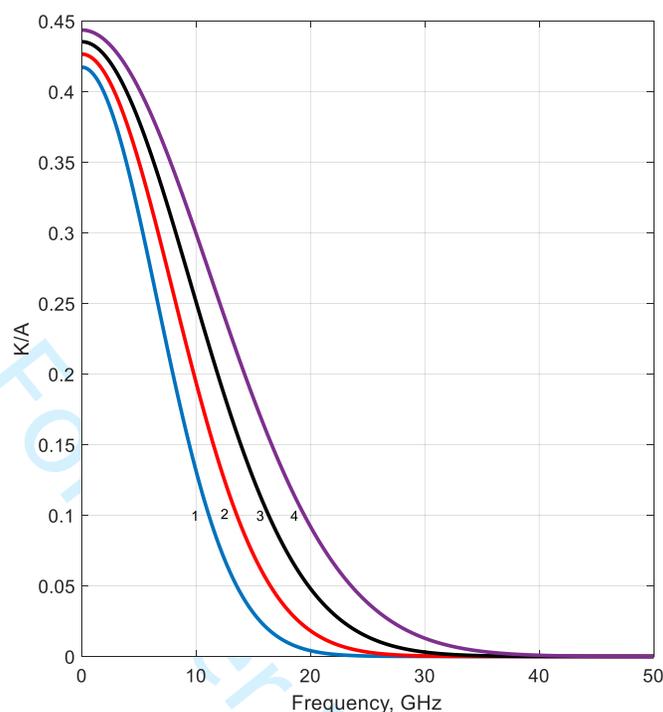


Fig. 4. Normalized Marcus rate coefficient K/A versus frequency (methanol) for different temperatures. Curves: 1- 298 K; 2 - 308 K; 3 - 318K ; 4 - 328K . $\Delta G_0/k_b T = 0.1$, $a_1 = a_2 = 5 \cdot 10^{-10}$ m, $R = 15 \cdot 10^{-10}$ m, $\Delta e = e = -1.602 \cdot 10^{-19}$ C, and $T = 298$ K .

These simple simulations show some new interesting effects in electron transfer reactions assisted by microwaves, but further research will need the semiclassical or quantum-mechanical simulations because of the known limitation of classical models providing analytical results. These limitations, for instance, are considered by Marcus in [1]. Several modifications of Marcus theory are known including calculation of quantum effects, and they are reviewed in [5]. Original theories are proposed in [6],[14],[15]. Besides known listed limitations, this original research is with the restrictions itself. For instance, the full system of equations for the rate coefficient calculation is solved in a very reduced manner, and it is obtained only for isothermal conditions with a given temperature. Besides, it is supposed a very low concentration of reagents in polar solvent approximated by a Debye mode for the sake of simplicity. Otherwise, these reagents and chemical dynamics can influence the reaction outcome, and microwave irradiation should be applied controllable in its power and frequency. For this purpose, more serious attention should

be paid on measurements of liquid permittivities during the microwave-assisted heating and chemical reactions [20],[24].

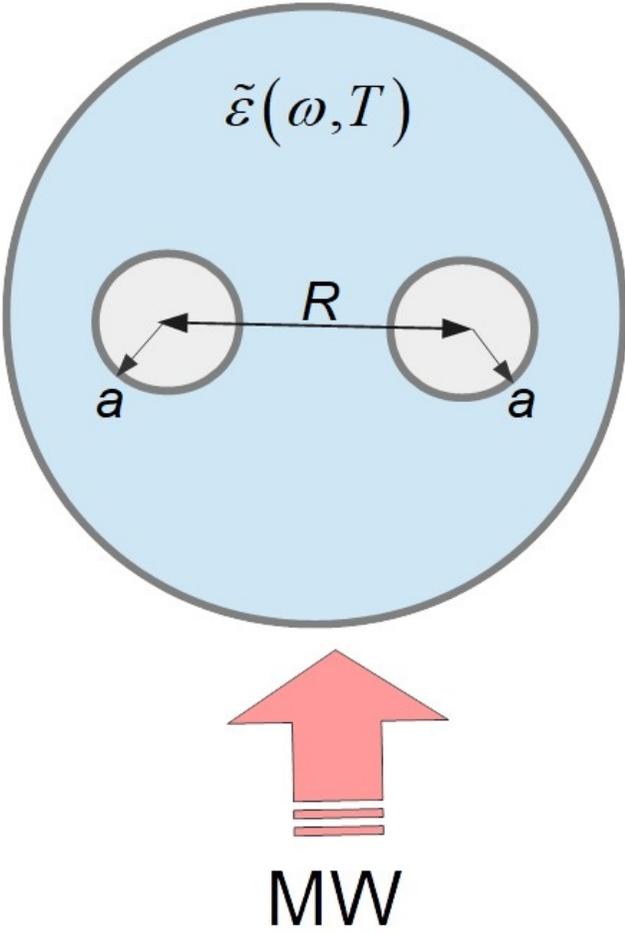
5. Conclusions

In this paper, it has been considered a modified Marcus theory for electron transfer chemical reactions in polar dispersive solvents heated by microwave irradiation. A system of non-linear equations has been formulated for microwave field, heating and liquid dynamics, and it is solved in for the isothermal reactions with the calculation of Marcus formula modified using the frequency- and temperature-dependent Pekar's factor. It has been shown that in the case of the smallness of the normalized reaction free energy $\Delta G_0/k_B T \ll 1$, the normalized reaction rate coefficient $k(T, \omega) = K/A$ is very high even in ambient condition, and the frequency bandwidth can reach several tenths of Gigahertz. The growth of $\Delta G_0/k_B T$ leads to essential decreasing this coefficient and reaction frequency. These parameters can be increased by temperature growth. This research has shown on the non-straightforward kinetics of electron transfer reactions in dispersive polar solvents in microwaves. There is a need in further theoretical and experimental studies to confirm the significance of found effects for practice, including the semi-classical and quantum-mechanical simulations in chemical reactors assisted by microwaves.

- [1]. R.A. Marcus, On the theory of electron-transfer reactions. VI. Treatment for homogeneous and electrode reactions, *J. Chem. Phys.*, **43**, 679-701 (1965).
- [2]. R.A. Marcus and N. Sutin, Electron transfers in chemistry and biology, *Biochimica et Biophysica Acta*, **811**, 265-322 (1985).
- [3]. R.A. Marcus, Electron transfer reactions in chemistry. Theory and experiment. *J. Rev. Mod. Phys.*, **65**, 599-610 (1993).
- [4]. A. Nitzan, *Chemical Dynamics in Condensed Phases*, Oxford Univer. Press, 2006.
- [5]. G. Likhtenshtein, *Solar Energy Conversation: Chemical Aspects*, Wiley, 2012.
- [6]. P.P. Dogonadze, A.M. Kuznetsov, and A.A. Chernenko, Theory of homogeneous and heterogeneous electronic processes in liquids, *Russ. Chem. Rev.*, **34**, 759 (1965).
- [7]. S.I. Pekar, *Study of electron theory of crystals (Issledovaniya po Ekektronnoj Teorii Kristallov*. GITTL, Moscow, 1951, in Russian). See as well S.I. Pekar, *Research in electron theory of crystals*, USAEC, Washington, D.C., 1963, Translation from Russian.
- [8]. F. Kishimoto, T. Imai, S. Fujii, D. Mochizuki, M.M. Maitani, E. Suzuki, and Y. Wada, Microwave-enhanced photocatalysis on CdS quantum dots - evidence of acceleration of photoinduced electron transfer, *Sci. Rep.*, **5**, 11308(1-8). 2015.
- [9]. H. Zhou, B. Liu, J. Sun, G. Xie, N. Ren, Z.J. Ren, and D. Xing, Pulse electromagnetic fields enhance extracellular electron transfer in magnetic bioelectrochemical systems, *Biotechnol. Biofuels*, **10**, 238, 2017.
- [10]. Y. Wada, S. Tsubaki, M.M. Maitani, S. Fujii, F. Kishimoto, and N. Naneishi, Physical insight to microwave special effects: Nonequilibrium local heating and acceleration of electron transfer, *J. Jap. Petrol. Inst.*, **61**, 98-105 (2018).

- 1
2
3 [11]. V.N. Peters, T.U. Tumkur, G. Zhu, and M.A. Noginov, Control of a chemical reaction (photodegradation of the p3ht
4 polymer) with nonlocal dielectric environment, *Sci. Rep.*, **5**, 14620(1-5) (2015).
5 [12]. G.G. Raju, *Dielectrics in Electric Fields*, Marcel Dekker Inc., 2003.
6 [13]. S.V. Kapranov and G.A. Kouzaev, Models of water, methanol, and ethanol and their applications in the design of
7 miniature microwave heating reactors, *Int. J. Thermal Sci.*, **122**, 53-73 (2017).
8 [14]. A.A. Ovchinnikov and M.Ya. Ovchinnikova, Contribution to the theory of elementary electron transfer reactions, *Soviet*
9 *Physics JETP*, **29**, 688-693 (1969).
10 [15]. L.D. Zusman, Dynamic effects of the solvents in the electron transfer reactions, *Russ. Chem. Rev.*, **61**, 15 (1992).
11 [16]. E.W. Castner, G.R. Flemings, and B. Bagchi, The dynamics of polar solvation: Inhomogeneous dielectric continuum
12 models, *J. Chem. Phys.*, **89**, 3519-3534 (1988).
13 [17]. A. Loupy (Ed.), *Microwaves in Organic Synthesis*, second ed., Wiley-VCH, Weinheim, 2006.
14 [18]. M. Larhed and K. Olofsson (Eds.), *Microwave Methods in Organic Synthesis*, Springer, Berlin, 2006.
15 [19]. C.O. Kappe, A. Stadler, and D. Dallinger, *Microwaves in Organic and Medicinal Chemistry*, second ed., Wiley-VCH,
16 Weinheim, 2012.
17 [20]. S.V. Kapranov and G.A. Kouzaev, Study of microwave heating of reference liquids in a coaxial waveguide reactor using
18 the experimental, semi-analytical and numerical means, *Int. J. Thermal Sci.*, **140**, 505-520 (2019).
19 [21]. G.A. Kouzaev, *Application of Advanced Electromagnetics. Components and Systems*, Springer, 3013.
20 [22]. S.V. Kapranov and G.A. Kouzaev, Nonlinear dynamics of dipoles in microwave electric field of a nanocoaxial tubular
21 reactor, *Mol. Phys.*, **117**, 489-506 (2019).
22 [23]. C.D. Abeyrathne, M.N. Halgamuge, P.M. Farrell, and E. Skafidas, An ab-initio computational method to determine
23 dielectric properties of biological materials, *Sci. Rep.*, **3**, 1796(1-5) (2013).
24 [24]. D.S. Campos, E.L. Dall'Oglio, P.T. de Sousa Jr., L.G. Vasconcelos, and A. Kuhnen, Investigation of dielectric properties
25 of the reaction mixture during the acid-catalyzed transesterification of Brazil nut oil for biodiesel production, *Fuel*, **117**,
26 957-965 (2014).
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



184x192mm (96 x 96 DPI)

Statement of article significance

In this manuscript, the frequency dependence of electron transfer chemical reactions assisted by microwaves is studied using the molecular theory of Marcus. In the first time, it is discovered non-thermal effects in increasing of normalized rate coefficient with microwaves at multi-ten Gigahertz range, and it is established the condition of existence of this effect. The temperature influence on microwave-assisted reactions of this type is considered. A formal algorithm for full-size simulation of these reactions is given. These theoretical findings are interesting in microwave-assisted accelerated chemistry.

For Peer Review Only