Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information 2

The microwave accelerates particles in their translations in z-axis, that is one freedom of motion in the six motions, namely, three translations and three rotations belongs to x, y and z-axis. In the following discussions, the velocity v denotes the translation velocity v_z. The Maxwell-Boltzmann velocity distributions function $f(v)$ is perturbed as shown in the second term in the following eq. (1),

$$f(v) = f_0(v) + f_0(v)(v - v_{ph})g(v). \quad (1)$$

The schematic view of the perturbation by intense microwave to Maxwell-Boltzmann is shown in Fig. 1.

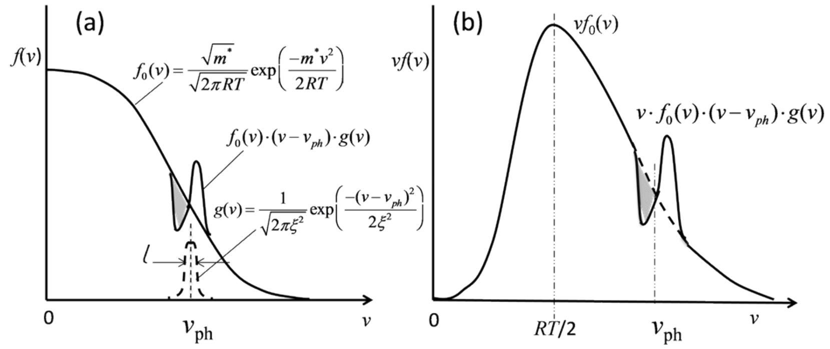

Figure 1. Perturbation by intense microwave to Maxwell-Boltzmann distributions

If the microwave is quite monochromatic, the perturbation takes a form of delta function in the velocity space. However, the delta fluctuation will spread in the velocity space by many kinds of disturbances. The delta function is approximated by Sync function described as $f_x(x)=\sin(kx)/\pi x$ that is well known form in the quasi-linear approximation of Landau damping. However, the cross term of $f_0(v)$ and $g(v)$ will need very complicated calculations. The other approximation of delta function is the normal function shown as;

$$g(v) = \frac{1}{\sqrt{2\pi\xi^2}} exp\left(\frac{-(v - v_{ph})}{2\xi^2}\right). \quad (2)$$

The form of eq. (44) is symmetric at $v = v_{ph}$. The variance ξ^2 corresponds to the velocity spread by the accumulation of ordered motions near median v_{ph} that synchronizes to the phase velocity of electro-kinetic wave.

The rate of chemical reactions are described by the Arrhenius plots as a function of temperature,

$$k = \alpha exp\left(\frac{-E_0}{RT}\right) \tag{3}$$

The rate of chemical reaction k is related to velocities passing by activation complex,

$A + B \rightleftharpoons X^{\ddagger} \rightleftharpoons C + D$

The transition state theories formulates the average velocity by the numbers of particles transmitting the activation complex $X^{\ddagger}$ as,

$$\overline{V}_f = \frac{\int_0^{\infty} vf(v)dv}{\int_0^{\infty} f(v)dv}. \tag{4}$$

Followed by Eyring, the rate constant k* between two molecules is

$$k^* = \frac{1}{2}\frac{\overline{V}_f}{\delta}k^{\dagger}. \tag{5}$$

Assuming the complexes are lying within the arbitrary length δ and the translational partition function, the rate functions $k^{\dagger}$ derives as

$$k^{\dagger} = \frac{q^{\dagger}}{q_a q_b}\frac{\sqrt{2\pi m^* RT}}{h}\delta exp\left(\frac{-E^*}{RT}\right). \tag{6}$$

Under the intense microwave irradiations, the average velocity of particles across the col of activated complex is calculated by substituting eq. (4) to eq. (1),

$$V_f = \frac{\int_0^{\infty} vf(v)dv}{\int_0^{\infty} f(v)dv} = \frac{\int_0^{\infty} vf(v)dv + \int_0^{\infty} vf_0(v - v_{ph})g(v)dv}{\int_0^{\infty} f(v)dv + \int_0^{\infty} f_0(v - v_{ph})g(v)dv}. \tag{7}$$

Although Detailed calculations are handed over to books [E. Guenin ed. S. Takayama, J. Fukushima, M. Sato, Microwave Engineering of Materials & Nanomaterials, Capter 1, *Pan Stanford Publishing*, (2016) ISBN978-9814669429], assuming the kinetic energy $m^*\xi^2/2$ in the induced vibration by microwave is much smaller than the thermal energy $RT/2$ in the system, and we get a form of average velocity of particles across the col of activated complex under intense microwave as

$$\overline{V}_f = \frac{\sqrt{m^*}}{\pi\sqrt{RT}}\left(\frac{RT}{m^*} + \xi^2\right). \qquad (8)$$

Substituting eq. (8) into eqs. (5) and (6), the rate function under intense microwave is concluded as,

$$k^* = \frac{q^\dagger}{q_a q_b}\left[\frac{RT}{h} + \frac{m^*\xi^2}{h}\right] exp\left(\frac{-E^*}{RT}\right). \qquad (9)$$

In eq. (54), the first term $RT=h$ in a bracket [ ] is the thermal reaction. The second term $m^*\xi^2/h$ is the kinetic energies of the ordered motions of molecules and lattices.