SHIFT OF CHEMICAL EQUILIBRIUM IN A RESONANCE INFRARED RADIATION FIELD

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The degree of displacement of chemical equilibrium in dissociation reactions, including three-particle recombination due to laser radiation at an isolated vibrational degree of freedom of the molecules, is determined. Dependences of the "vibrational temperature" and the chemical equilibrium constant on the vibrational excitation probability are obtained.

The theoretical possibility of varying the rate of a chemical reaction as infrared laser radiation is absorbed by a molecular gas was demonstrated in [1-10]. A variation in the rates of chemical reactions invariably leads to a shift of chemical equilibrium into a resonance laser radiation field.

Displacement of chemical equilibrium was first considered in [11] for a dissociation reaction in a system with a non-Maxwellian rate distribution due to a source of energetic particles that "heated up" the vibrations.

The "displaced chemical equilibrium constant" $\varkappa(T, \theta_v) = N^2_A/N_M$ corresponding to the steady-state dissociation reaction of three-particle recombination occurring with resonance laser radiation at the vibrational levels 0 and 1 with absorption W_{01} and radiation W_{10} probabilities ($W_{01} \approx W_{10}$) (N_M and N_A are the densities of the number of molecules and atoms, that is, the reaction products in the final steady state) is defined for a system of truncated harmonic oscillators. The equations for the vibrational temperature T_V and concentrations N_M and N_A have the form, * given that dissociation and recombination are in dynamic equilibrium,

$$(\alpha - \alpha_T)/\tau_{vt} = W_{10}(y_0 - y_1); \tag{1}$$

$$2N_M + N_A = N_0 = \text{const};$$

$$N^2_A/N_M = \varkappa(T, \theta_v) = \varkappa(T)\left(1 - e^{-\theta_v}\right)\left(1 - e^{-\theta T}\right)e^{m(\theta_v - \theta_T)},$$

where $\theta_v = h\nu/kT_V$, $\theta_T = h\nu/kT$, ν is the frequency of molecular vibrations, T is the temperature of translational degrees of freedom, which is assumed constant, α_T and α are the reserves of vibrational quanta corresponding to the temperatures T and T_V, y_0 and y_1 are the relative populations of the vibrational levels 0 and 1, $\varkappa(T)$ is the chemical equilibrium constant in the absence of laser radiation, and m is the number of a discrete boundary level $(m \gg 1)$.

The relaxation time τ_{vt} occurring in Eqs. (1) depends on N_M and N_A,

$$\tau_{vt}^{-1} = \left(1 - e^{-\theta T}\right)\left(N_M P^M_{10} + N_A P^A_{10}\right),$$

where P^M_{10} and P^A_{10} are the number of $1 \to 0$ transitions within a unit of time as a single molecule collides with molecules or atoms, referred to a unit concentration of collision partners. Usually, $P^A_{10} \gg P^M_{10}$, so that the nature of vibrational relaxation will vary as the degree of dissociation of the gas increases.

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*Since the vibrational distribution function is distorted at the levels 0 and 1 by optical pumping, the relation between α and T_V is more complex (in the general case) than in the case of a Boltzmann distribution, which occurs for levels above the first [1, 7].
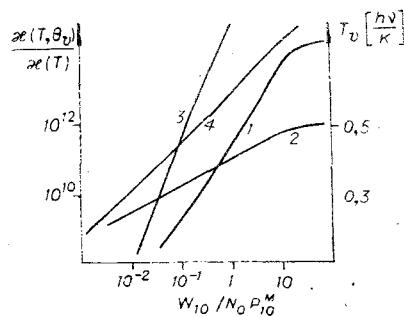

Fig. 1

For illustration, we first consider the highly unsaturated regime of optical pumping (the condition $W_{10} \ll N_M Q_{10}$, where Q_{10} is the probability of the $0 \to 1$ and $1 \to 0$ vibrational-vibrational transitions within a unit of time as two molecules in the zero and first vibrational states collide, referred to a single particle and unit concentration of collision partners). In this case, we find that when $\theta_v \gg 1$ and when $N_A P_{10}^A \ll N_M P_{10}^M$,

$$\theta_v \approx \theta_T - \ln\left(1 + \frac{2e^{\theta_T} W_{10}}{N_0 P_{10}^M}\right); \quad \frac{\varkappa(T, \theta_v)}{\varkappa(T)} \approx \left(1 + \frac{2e^{\theta_T} W_{10}}{N_0 P_{10}^M}\right)^m; \tag{2}$$

while when $N_A P_{10}^A \gg N_M P_{10}^M$, $N_A \ll N_M$

$$\theta_v \approx \frac{2}{2+m} \ln\left\{W_{10}^{-1}\left[\frac{\varkappa(T) e^{m\theta_T}}{2N_0}\right]^{1/2}\right\}; \tag{3}$$

$$\frac{\varkappa(T, \theta_v)}{\varkappa(T)} \approx e^{m\theta_T} W_{10}^{\frac{2m}{2+m}}\left(\frac{\varkappa(T)}{N_0} e^{m\theta_T}\right)^{-\frac{m}{2+m}};$$

and when $N_A P_{10}^A \gg N_M P_{10}^M$; $N_A \gg N_M$

$$\theta_v \approx \theta_T - \ln\left(1 + \frac{e^{\theta_T} W_{10}}{N_0 P_{10}^A}\right); \quad \frac{\varkappa(T, \theta_v)}{\varkappa(T)} \approx \left(1 + \frac{e^{\theta_T} W_{10}}{N_0 P_{10}^A}\right)^m. \tag{4}$$

It is evident from Eqs. (2)-(4) that the chemical equilibrium constant $\varkappa(T, \theta_v)$ depends in the laser radiation field on radiation intensity and can significantly exceed its equilibrium value $\varkappa(T)$.

Saturation conditions, under which the rate of energy influx to the vibrational degree of freedom of the molecules is limited by the rate of intermolecular energy exchange, is attained when $W_{10} \gg M_M Q_{10}$. When $\theta_v \gg 1$ and $N_A P_{10}^A \gg N_M P_{10}^M$, we have

$$\varkappa(T, \theta_v) \approx \frac{3}{4} e^{\theta_v} \frac{Q_{10}}{P_{10}^A} N_0; \quad \theta_v \approx \frac{1}{m+1} \ln\left[\frac{4\varkappa(T) e^{m\theta_T} P_{10}^A}{3N_0 Q_{10}}\right].$$

The equilibrium constant is independent of pumping power and maximally differs from its equilibrium value under saturation conditions. The dependence of $\varkappa(T, \theta_v)/\varkappa(T)$ (curve 1) and of the vibrational temperature (curve 2) on the probability W_{10} is illustrated in Fig. 1 for $m = 6$, $Q_{10}/P_{10}^M = 10^3$, $P_{10}^A/P_{10}^M = 10^2$, $N_0 = 10^{16}$ cm^{-3}, and $\theta_T = 7$. Values of $\varkappa(T, \theta_v^*)/\varkappa(T)$ (curve 3) calculated using theoretical values of T_v^* (curve 4) characteristic for the initial stage of dissociation are depicted for comparison.

The substantial difference between $\varkappa(T, \theta_v)$ and $\varkappa(T, \theta_v^*)$ is due to the difference between the initial and final (steady-state) values of θ_v (curve 2). This indicates the need for tracing the development of the kinetics in time and for taking into account the variation in gas composition and rate in the course of the reaction in considering the kinetics of chemical reactions due to radiation without limiting ourselves to the initial time intervals, as has been done until now.

In conclusion, we wish to note that all our results remain in force for other methods of exciting vibrations (for example, for electrical pumping).

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