

THERMAL EXPLOSION DURING LASER DISSOCIATION OF MOLECULAR GAS

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The kinetics of diatomic molecule photodissociation under laser irradiation is studied theoretically for the case where heat exchange exists between the gas and the ambient medium. The mode of thermal explosion in such a system is discovered and investigated. The behavior of the entropy production function in the photodissociation process is analyzed.

Laser dissociation of a molecular gas is a nonlinear process which, depending on the intensity of laser radiation, may proceed in different modes. Mode switching occurs in an explosive manner (the thermal explosion) and is accompanied by abrupt temperature changes. The goal of the present paper is to analyze the possible modes and threshold effects in laser dissociation of molecular gases. The latter is important for laser radiation propagation in a dissociating medium and determines the choice of optimum conditions for photochemical reactions. In contrast to thermal explosions during chemical reactions [1, 2] and under nonequilibrium vibrational excitation of diatomic molecules [3, 4], studied earlier, the process in question is related to photodissociation in the visible or UV radiation bands.

The physical model of the phenomenon at hand is as follows. A homogeneous gaseous medium is subjected to external laser pumping of intensity I , exchanging its heat with the ambient medium by the law $\alpha(T - T_0)$, where T_0 is the temperature of the medium. It is assumed that heat exchange and laser pumping do not disrupt the system homogeneity. The gas molecules are modeled by truncated harmonic oscillators with natural frequency ω , whose vibrational energy has a Boltzmann distribution with a vibrational temperature different from that of the translational degrees of freedom (an infinitely fast VV -exchange).

The following scheme of dissociation is considered.

1. After the absorption of an external radiation quantum, the molecule photodissociation occurs from the m th quantum level.
2. Collisional dissociation is negligibly low.
3. Recombination processes occur when two atoms collide with a third particle (an atom or a molecule), the processes of photorecombination being less effective.

During photodissociation, the emerging atoms have an effective temperature T_a defined by

$$\hbar\tilde{\omega} = D - m\hbar\omega - (5/2)kT + 3kT_a,$$

where $\hbar\tilde{\omega}$ is the energy of the external radiation quantum and D is the molecule dissociation energy. The value of T_a may be both higher and lower than the gas temperature T , depending on the value of $\hbar\tilde{\omega}$. In the first case the gas is heated and in the second case it is cooled. The gas temperature time course depends on the relative magnitudes of the heat release and heat removal rates, which vary with time. Several modes are possible. For low pumping intensities I , the rate of heat release inside the system is comparable to that of heat exchange, and with time the system smoothly reaches a stationary mode in which the gas temperature grows with I . As I is further increased, particularly after having reached the threshold level, the heat release rate and the gas temperature grow abruptly, which leads to a sharp increase in the external absorption and, as a consequence, to an avalanche growth of the gas temperature. As a result of this thermal explosion, the system transforms into a new stationary mode which is stable. When the intensity I is increased still further, the stationary gas temperature ceases to depend on I and a saturation effect is observed.

This model of photodissociation is described by the following set of nonlinear differential equations

$$\frac{d}{dt} \left[N \left(\frac{5}{2} kT + D \right) + n \left(\frac{3}{2} kT + D \right) + N \frac{\hbar\omega}{\exp\left\{\frac{\hbar\omega}{kT_v}\right\} - 1} \right] = \hbar\tilde{\omega} W N_m - \alpha(T - T_0), \quad (1)$$

$$\frac{d}{dt} \left[N \frac{\hbar\omega}{\exp\left\{\frac{\hbar\omega}{kT_v}\right\} - 1} \right] = -\frac{1}{\tau_{VT}} N \hbar\omega \left[\frac{1}{\exp\left\{\frac{\hbar\omega}{kT_v}\right\} - 1} - \frac{1}{\exp\left\{\frac{\hbar\omega}{kT}\right\} - 1} \right] - m\hbar\omega W N_m + k\hbar\omega P_{dl}(N + n)n^2, \quad (2)$$

$$\frac{d}{dt} N = -W N_m + P_{dl}(N + n)n^2. \quad (3)$$

Here t is the time, T_v is the vibrational temperature, k is the Boltzmann constant, N and n are the concentrations of molecules and atoms, P_{dl} are the probabilities of atom recombination producing a molecule on level l , W is the probability of molecule photodissociation from the m th quantum state, and τ_{VT} is the time of vibrational relaxation. The following auxiliary relations are employed.

1. $2N + n = R$, where R is a constant equal to the concentration of the bound and free atoms in the system.

$$2. N_m = N \left(1 - \exp\left\{-\frac{\hbar\omega}{kT_v}\right\} \right) \exp\left\{-\frac{m\hbar\omega}{kT_v}\right\},$$

where N_m is the concentration of molecules in the quantum state m .

3. $1/\tau_{VT} = N/\tau_m^0 + n/\tau_a^0$, where τ_a^0 and τ_m^0 are the vibrational energy relaxation times for collisions of molecules with atoms and molecules, respectively, per unit concentration of molecules and atoms. The relaxation time τ_m^0 is usually determined by the Landau-Teller formula, but in some cases empirical dependencies are used. For instance, for an NO molecule

$$\tau_m^0 = \exp\left\{-\frac{T}{1200}\right\} 10^{13} \text{ s.}$$

For an estimate of τ_a^0 , one may set

$$\tau_a^0 = \tau_m^0/10.$$

Equation (1) describes the system's energy balance. The first term on the right-hand side corresponds to the energy flow coming into the system by radiation, the second term is the energy that leaves the system as a result of heat exchange with the ambient medium. Equation (2) describes the system's vibrational energy balance. The first term on the right-hand side characterizes the change in the vibrational energy due to the process of translation-vibration energy exchange in collisions (the VT-exchange), the next terms are the changes due to, respectively, photodissociation and collisional recombination. Equation (3) describes the change in the number of particles in the system under dissociation and recombination. In the initial time the system is assumed to have been in equilibrium with the ambient medium — that is, $T = T_0$ — and the initial concentration was assumed to be 10^{17} cm^{-3} .

Let us perform a qualitative analysis of the set (1)–(3). At the initial heating stages, when the translational and vibrational temperatures are little different from T_0 , the system can be linearized. The linearized equation in $\Delta T = T - T_0$ has the form

$$\frac{d\Delta T}{dt} \cdot k = A\Delta T + B, \quad (4)$$

where

$$B = \frac{H}{\tau_0} \exp\left\{-\frac{m\hbar\omega}{kT_0}\right\} \left(m\hbar\omega - D + \hbar\tilde{\omega} - \frac{1}{2}kT_0 \right),$$

$$A = \left\{ \frac{H}{\tau_0} \exp\left\{-\frac{m\hbar\omega}{kT_0}\right\} \cdot \left[\frac{1}{2}k + m\frac{\hbar\omega}{kT_0^2} (m\hbar\omega - D + \hbar\tilde{\omega}) \right] - \frac{\alpha}{N} \right\},$$

$$H = W\tau_0, \quad \tau_0 = \tau_{VT} \sim 10^{-5} \text{ s for } T = \frac{\hbar\omega}{k}.$$

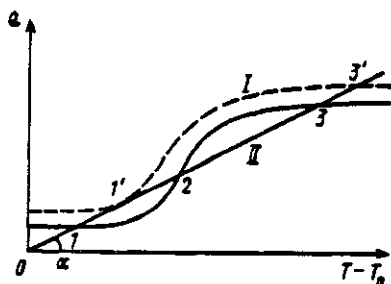


Fig. 1

Schematic illustration of the incoming (Q_I) and outgoing (Q_{II}) energy flows in the system as functions of $\Delta T = T - T_0$.

It was assumed for the derivation that $\frac{m\hbar\omega}{kT_0} \frac{\Delta T}{T_0} \ll 1$. As is seen from (4), the condition $A = 0$ divides the regions of stable and unstable solutions. For small H , which correspond to low values of the intensity I ($H = 2\pi\sigma\tau_0 I / \hbar\tilde{\omega}$, where σ is the cross section of laser radiation absorption), the solution is always stable. With growing I and $A \rightarrow 0$, the solution becomes unstable. The nature of this instability can be understood by considering (1). The two terms from the right-hand side of (1), describing the incoming (Q_I) and outgoing (Q_{II}) energy flows, are plotted in Fig. 1. In the coordinates $T - T_0$, the quantity Q_{II} is depicted by straight line II whose inclination tangent is α , while Q_I is depicted by curve I which, in general, may intersect line II at several points (see Fig. 1). For small ΔT , the incoming energy flow is greater than the outgoing one ($Q_I > Q_{II}$) and the gas undergoes heating. This heating stops at point 1 where $Q_I = Q_{II}$. A stationary stable state corresponds to point 1 (under fluctuations ΔT the system returns to point 1). To point 2, where again $Q_I = Q_{II}$, there also corresponds a stationary state, but it is unstable (under fluctuations ΔT the system transforms from state 2 to state 1 or state 3). Point 3 again corresponds to a stationary stable state.

As the radiation intensity — that is, the value of H — is raised, curve I goes upward and points 1 and 2 merge at point 1'. An unstable stationary state is created, from which the system passes into a new stable stationary state 3'. The threshold of instability is determined by the condition $dQ_I/d\Delta T = dQ_{II}/d\Delta T$ and corresponds to $A = 0$. Note that within the approximation considered here one may speak of a stationary mode for T and T_0 , because, even neglecting recombination, this mode settles earlier than all the molecules dissociate.

The threshold values of $H^* = 2\pi\sigma\tau_0 I^* / \hbar\tilde{\omega}$ for the particular conditions $\frac{\alpha}{Nk} = 0.4$, $m - \frac{D}{\hbar\omega} + \frac{\tilde{\omega}}{\omega} = 10$, $m = 3$, $\sigma = 10^{-18} \text{ cm}^2$, $\tilde{\omega} = 1.02 \times 10^{16} \text{ s}^{-1}$, $\omega = 3.58 \times 10^{14} \text{ s}^{-1}$, and $D = 5.29 \text{ eV}$ are listed in Table 1.

Table 1

T_0 , K	500	700	900	1000	2000
H^*	7477	115	13	7	0.43
I^* , $\frac{\text{kJ}}{\text{cm}^2}$	43	6.5	0.74	0.39	0.024

Detailed analysis of the system behavior in the vicinity of H^* can be carried out by a numerical solution of the system (1)–(3). Figure 2 shows time dependences of T and T_0 for $T_0 = 826 \text{ K}$ and for different H . With $H < H^*$ (for $T_0 = 826 \text{ K}$, $H^* = 26$), constant laser irradiation leads to gradual heating of the system (curve 1). However, the monotonic heating pattern breaks down as soon as the radiation intensity becomes

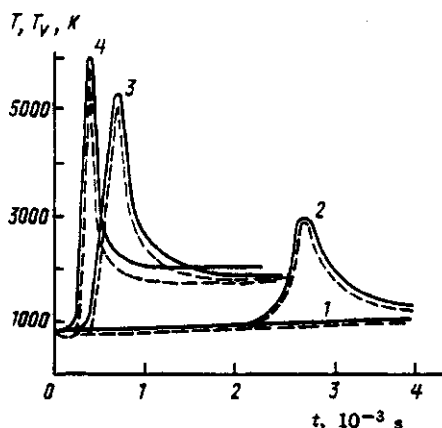


Fig. 2

Time dependence of T (solid curves) and T_v (dashed curves) for $H = 20$ (1), 30 (2), 70 (3), and 250 (4).

greater than the threshold value (curves 2, 3, and 4, for which $H > H^*$). The appearance of a peak on the temperature curves corresponds to thermal explosion. In this case, the energy released by photodissociation has no time to be removed to the external medium. An abrupt system heating occurs which increases the intensity of heat exchange with the ambient medium, and this restricts any further growth of the temperature. As is seen in Fig. 2, as the laser radiation intensity grows, the thermal explosion is localized in time and the temperature peak becomes higher and narrower. The stationary value of the gas temperature grows with H (Fig. 3). The abrupt change in the vibrational temperature also leads to a sharp change in the absorption coefficient. This effect must be taken into account when analyzing the propagation of laser radiation, because it may give rise to spatial and temporal modulation of the light beam intensity. When H (or the radiation intensity I) is increased further, the stationary-state temperature ceases to depend on H . The saturation mode sets in. This effect can be understood if one bears in mind the fact that at high I the bottleneck in the photodissociation process is particle supply to the m th vibrational level, rather than the transition from the m th level into the continuous spectrum due to photodissociation. The rate of molecule excitation at the m level does not depend on I and is solely determined by the rate of the VT-exchange.

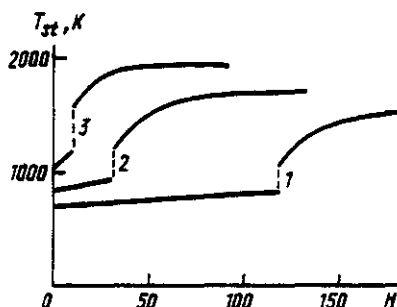


Fig. 3

Stationary temperature as a function of H for $T_0 = 700$ K (1), 800 K (2), and 1000 K (3).

The condition $A = 0$ can be written as

$$\frac{H}{\tau_0} \exp\left\{-\frac{m\hbar\omega}{kT_0}\right\} \left[km\left(\frac{\hbar\omega}{kT_0}\right)^2 \left[m - \frac{D}{\hbar\omega} + \frac{\tilde{\omega}}{\omega} \right] \right] = \frac{\alpha}{N_0}. \quad (5)$$

In the space of the initial values of density N and temperature T_0 for $H = \text{const}$, Eq. (5) defines a curve which separates the region of thermal explosion from that of stable monotonic heating. Thus Eq. (5) is the curve of a nonequilibrium phase transition, separating two different dissipative structures. In nonequilibrium thermodynamics, a dissipative structure is characterized by entropy production.

Entropy production σ in a stationary state has the form

$$\sigma = -\frac{N\hbar\omega}{\tau_{VT}} \left(\frac{1}{\exp\left\{\frac{\hbar\omega}{kT_v}\right\} - 1} - \frac{1}{\exp\left\{\frac{\hbar\omega}{kT}\right\} - 1} \right) \left(\frac{1}{T_v} - \frac{1}{T} \right) + \left(\frac{T - T_v}{T_v} \frac{\hbar\omega}{T} + \frac{D}{T} \right) P_{dl} n^2 (N + n).$$

This equation can be derived from the formula for the rate of variation of the total system entropy by omitting the terms related to pumping and heat exchange and retaining those responsible for the VT-exchange and recombination.

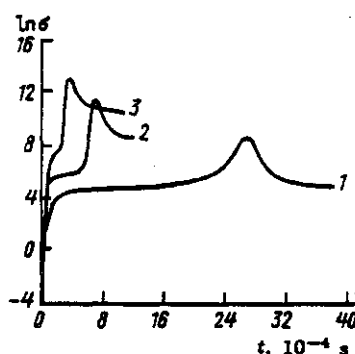


Fig. 4

Time dependence of $\ln \sigma$ for $H = 30$ (1), 70 (2), and 250 (3).

Figure 4 shows the time dependence of entropy production in the process of thermal explosion. The entropy production rises sharply at the instant of explosion, then assumes a stationary value which is greater than the corresponding value before the explosion.

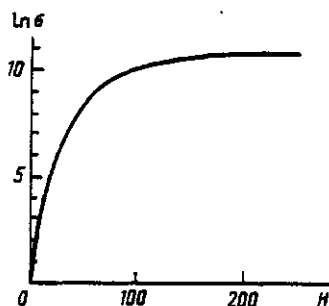


Fig. 5

Entropy production as a function of H .

Thus, the new structure created after the explosion is characterized by a higher level of entropy production. Figure 5 shows stationary-state entropy production as a function of H . Aside from the fact that σ is growing, Fig. 5 enables the following general conclusion to be drawn: the value of σ in the new structure turns out to be lower than the entropy production which could have existed in the system if there were

no restructuring. From the standpoint of the entropy production criterion [5], the new structure is more ordered. Thus in the competitive struggle of the two structures the mode with smaller dissipation wins — that is, becomes stable. The poorer organized structure turns out to be unstable. This conclusion agrees with the principle of least entropy production in the self-organization process that has been introduced in [5].

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