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EXPERIMENTAL APPROACH TO DISSIPATIVE PROCESS: TRAJECTORY TRACING IN COMPLICATED CHEMICAL REACTION SYSTEM

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The present study has introduced a new approach for the investigation of the complicated batch reaction system. This method is based on the spectrum theory and the stability theory. It was applied to the analysis of the typical temporal-evolution observed in the laser-induced aerosol formation from gaseous CS_2 molecules.

In the study of chemical reactions, while the experiments on their elementary processes are very important, the investigations on their macroscopic features are also of great interest, because the choice of trajectories is stochastic and cooperative phenomena are expectable in the complicated reaction system. The theoretical approach with the aid of the nonlinear mathematical techniques, i.e., the bifurcation, catastrophe, and stability theories, has been successful to understand the macroscopic features of chemical reactions.[1] Especially, the concepts "dissipative structure", " self-organization", "bifurcation", "stability", etc. have successfully explained interesting chemical reactions such as Belouzov[2]-Zhabotinski[3,4] reaction, biological reactions, enzyme catalyses, etc.[1] Nevertheless, such a theoretical macroscopic approach is limited in simple chemical reactions. The present study has introduced a new approach, in which the spectral distribution of the solutions of the differential equations of a complicated chemical reaction is obtained experimentally with the aid of the spectrum theory and interpreted on the basis of the nonlinear mathematical conceptions, for the study on the laser-induced aerosol formation reaction from gaseous CS_2 molecules. We refer to this approach as *trajectory tracing*.

An N_2-laser (Lambda Physik, EMG 102) beam was introduced into a reaction cell, which was a pyrex-glass sphere with 25-cm diameter and had two glass-sealed quartz windows, without focusing. The maximum power of the nitrogen laser was 1 MW and the repetition rate was 25 Hz. The aerosol formation was monitored by the measurement of the scattered light intensity of the blue-line emission of a He-Cd laser, with the use of a monochromator (Jobin Yvon, H20), a photomultiplier (Hamamatsu-TV, R106), a lock-in amplifier (PAR model 126), and a chart recorder. More details of the experimental procedure are available elsewhere.[5]

Figure 1 shows the temporal evolution of the scattered light intensity of the He-Cd laser. The intensity steeply increases with the time lapse until it gets to the peak and thereafter rapidly decreases. After 100 min of the N_2-laser irradiation time, the long period (approx. 300 min) oscillation is observed. Al-

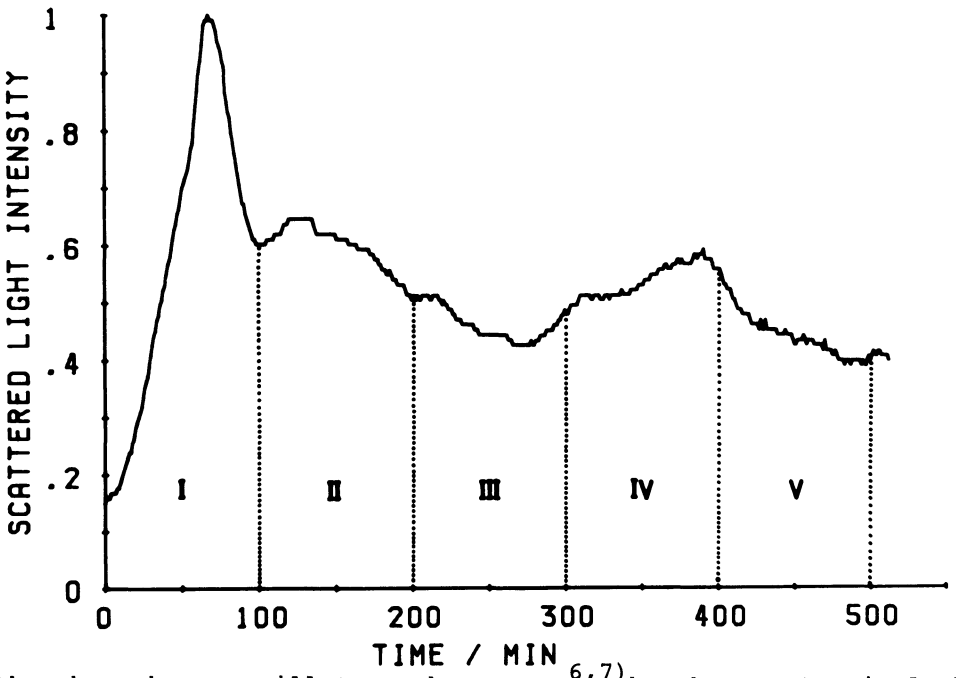


Fig. 1. Scattered light intensity as a function of the N_2-laser irradiation time. The CS_2 pressure is 69 Torr. (One Torr is equal to 133.322 Pa).

though such an oscillatory phenomenon[6,7] has been extensively known in various reaction systems, it has been incomprehensible, probably because of the complexity of the reaction system. Namely, the number of the species, which are formed in the present reaction system by the bimolecular photodissociation[8] of CS_2 molecules and various kinds of radical reactions, can be roughly estimated to be more than 10^{12}, i.e. the ratio of the volumes between an aerosol particle (a few μmϕ) and a CS_2 molecule (a few Åϕ).

The temporal evolution of the reaction system can be represented by Eq.1,

$$\frac{\partial \rho_i}{\partial t} = -\mathrm{div}\ \hat{J}_i + \Sigma_p\ \nu_{ip} W_p \qquad (i=1,2,3,\ ---,\ n), \tag{1}$$

where ρ_i is the composition variable, $\hat{J}_i$ the diffusion flux, W_p the reaction rates per unit volume, ν_{ip} the stoichiometric coefficients and t the N_2-laser irradiation time. These simultaneous differential equations are too complex to be solved by any theoretical method. However, based on linear stability analysis, the scattered light intensity, x, which can be regarded as a composition variable, will be approximately expressed by Eq.2 near the equilibrium,[1,5]

$$x = \Sigma_m\ a_m \exp(\omega_m t)\ u_m, \tag{2}$$

where a_m is the coefficient, $\exp(\omega_m t)$ the term for the time structure, and u_m the term for the spatial structure of the system. The stability and the periodicity of the trajectory of the reaction system are known to depend upon whether ω_m is positive or negative and real or imaginary, respectively.[1] A lot of nonlinear autonomous systems often show the almost periodical oscillations after the sufficiently long time-lapse, i.e. a limit cycle.[1] Therefore, as long as we can know the distribution and the periodicity of ω_m by some method, the reaction trajectory can be traced and interpreted with the aid of these conceptions based on the stability theory.

To manifest the distribution and the periodicity of ω_m, we calculated the power spectrum and the correlation function by using the time-series data of Fig.1.

The maximum entropy method[9] was applied to these calculations. To display the temporal changes of the spectrum and the correlation function, the calculations were made for each region, i.e. regions I-V. The results, i.e. the time-resolved spectrum and correlation function obtained, are shown in Fig.2 and can be interpreted as follows. In region I, the decreasing profile in the frequency range of 0-0.1 min^{-1} is in principle the superimposition of the exponential growth and decay accompanied by weak oscillations. In fact, the semilogarithmic plot of the temporal evolution of the scattered light intensity has confirmed that the exponential growth and decay rates are both approx. 0.2 min^{-1}. Therefore, the weak-oscillatory instability occurs in region I, i.e., the real and imaginary parts of ω_m are positive and nonzero, respectively, in Eq.2.[1] On the other hand, various

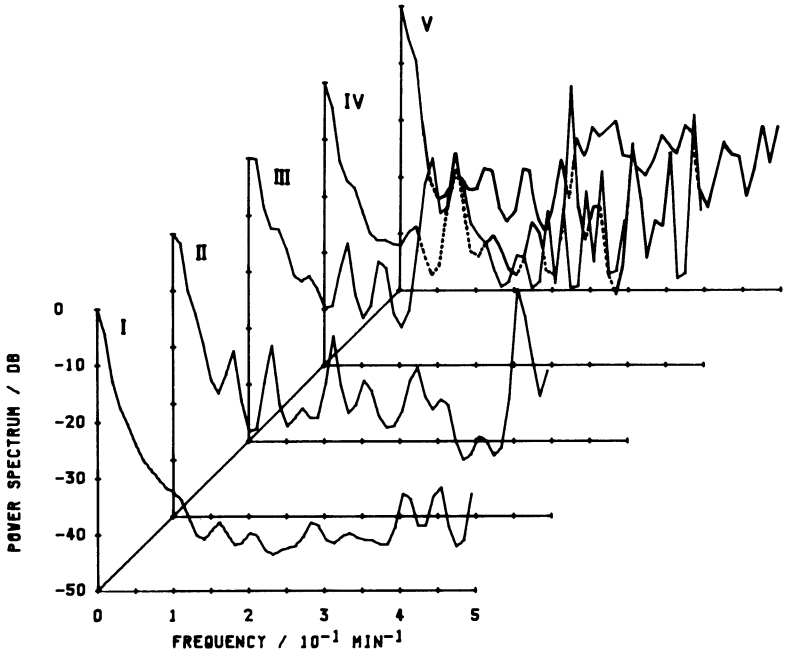
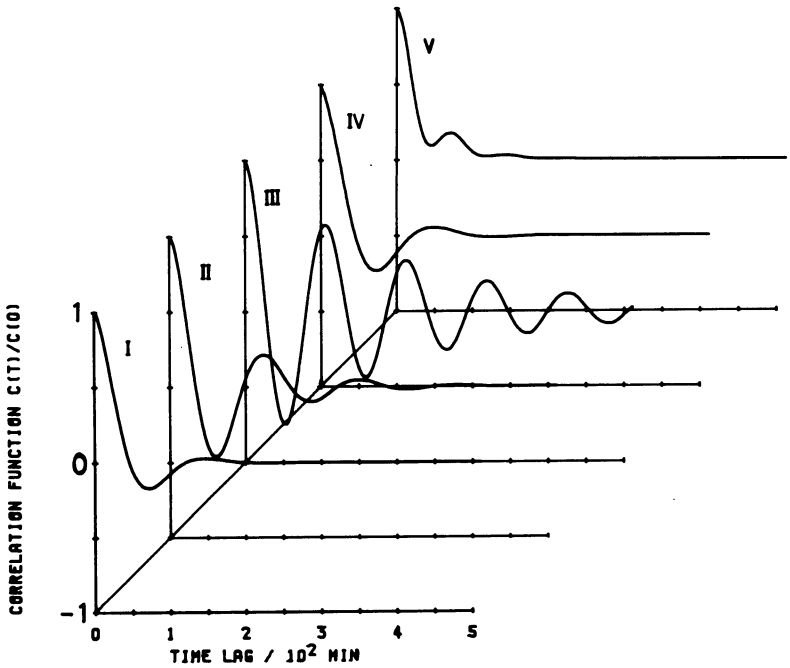


Fig.2.
(a) Time-resolved power spectrum for regions I-V: calculated by the maximum entropy method. The number of the prediction filters was 25. The number of time-series data was 100 for each region.



(b) Time-resolved correlation function for regions I-V: calculated by the maximum entropy method. The number of the prediction error filters was 25. The number of time-series data was 100 for each region.

oscillations arise in regions II-V. The strong bands, which appear in the frequency range between 0 and 0.01 min^{-1} in the spectra of regions II-V, are due to the slow oscillation (approx. 300-min period) observed in the time-evolution curve in Fig.1. In the frequency range higher than 0.1 min^{-1}, high-frequency oscillations appear and disappear successively; the spectrum becomes "white".

Thus, in regions II-V, we could confirm the existence of two kinds of oscillations which are essentially different each other; the long-period (approx. 300 min) oscillation and the high-frequency (higher than 0.1 min^{-1}) oscillation that causes the "whitening" of the spectrum. The period of slow oscillation turned out to be sensitive to the size of the reaction cell,[5] which suggests that the slow oscillation is relevant to the diffusion flux. On the other hand, the high-frequency oscillation will be probably subject directly to the "chemical reactions". In the present experiment, while the strong oscillation with the frequency of approx. 0.26 min^{-1} appears in region III, for example, it disappears and other oscillations arise in other regions. However, in a series of our experiments, we could often observe the bursting phenomena, which are due to the semistable limit cycle.[5] Namely, the high-frequency oscillations can form a more-stable periodic dissipative structure under some conditions.

In conclusion, the combination of the spectrum theory and the stability theory turned out to be very effective for the tracing and the interpretation of the trajectories of complicated chemical reactions, irrelatively to whether they were periodical or not, and by the application of this methodology we could explain the temporal evolution observed in the laser-induced aerosol formation in view of the dissipative process. Furhter details of this study, e.g. the investigation on the stability of the long-period oscillation, etc., will be published later. While the study on these complicated chemical reactions has been made passively in the past, we hope that the present approach will stimulate it.

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