6. Application of the Photoacoustic Effect to Studies of Gas Phase Chemical Kinetics

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With 23 Figures

Over the last decade, a number of applications of the photoacoustic effect to studies of chemical kinetics have appeared in the literature. From this work it is clear that the photoacoustic effect, perhaps as a result of its inherent high sensitivity and selectivity, is a welcome addition to the rather limited number of diagnostic methods chemists have for unravelling complex chemical reaction mechanisms. In addition to analytical applications, a few experimental methods based on the response of the photoacoustic effect to evolved heat have been developed. In pulsed experiments the rate of heat evolution determines the shape of the acoustic waveform; equally, in a modulated, continuous wave experiment the pathways for heat liberation determine the amplitude and phase of the sound wave. Perhaps the response that is most characteristic of chemical reactions vis-a-vis purely physical processes is the liberation of an amount of heat by the absorption of a photon that can exceed the energy of the photon itself. In such cases of the "chemically amplified" photoacoustic effect, the properties of the chemical reaction become paramount in determining the amplitude and phase of the acoustic wave. The object of this review is to summarize photochemical energy release mechanisms insofar as they relate to sound wave production as well as to recount the analytical applications of the photoacoustic effect to gas phase chemical kinetics; the wide range of phenomena and novel effects uncovered over the last several years make the subject of this review pleasing from a scientific viewpoint and suggest this area for further inquiry.

6.1 Pulsed Excitation

6.1.1 Signal Description

In general, the absorption of short-wavelength radiation results in the production of an excited molecular electronic state. Eventually the excitation energy is lost as a result of fluorescence, internal energy conversion to other states, energy transfer through collisions with other molecules, or molecular photodissociation. Only the last of these is an inherently chemical process in that a bond is broken. Although the process of photodissociation itself produces sound waves as a result of a local increase in mole number and through thermalization of the recoil energy of the fragments, the more interesting possibility is the initiation of chemical reactions, which release their own characteristic energy. The time scales for photofragmentation and chemical reaction are generally quite disparate.
todissociation of a diatomic molecule, for instance, may take place on a subpicosecond time scale; the rate of chemical reaction, on the other hand, depends on the pressure of the reactants and the reactivity of the species themselves, and may proceed at anywhere from the gas kinetic rate to an infinitesimally slow rate.

The production of sound waves by the evolution of heat, whether it be through chemical or physical processes, is a problem in fluid dynamics where the excess pressure \( p(r, t) \) is found (for negligible heat conduction) as a solution to the wave equation \([6.1]\),

\[
 \left( \gamma^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) p(r, t) = -\frac{\beta}{C_p} \frac{\partial}{\partial t} H(r, t), \tag{6.1.1}
\]

where \( c \) is the sound speed, \( \beta \) and \( C_p \) are the isobaric volume expansion coefficient and heat capacity, respectively, of the gas, and \( H(r, t) \) is the rate of heat evolution per unit volume at a point \( r \) at time \( t \). For a perfect gas, \( \beta \) is equal to \( 1/T \), the inverse of the temperature. By making use of the relation \([6.2]\)

\[
 \gamma - 1 = \frac{T \beta^2}{\kappa_s C_p \rho}, \tag{6.1.2}
\]

where \( \kappa_s \) is the isentropic compressibility and \( \rho \) the density, the proportionality constant \( \beta/C_p \) on the right-hand side of (6.1.1) can be written as \( (\gamma - 1)/c^2 \), where \( \gamma \) is the ratio of the heat capacity at constant pressure to that at constant volume. When the heat evolution is defined by only the temporal and spatial profile of the laser, in a cylindrically symmetric geometry the right hand-side of Eq. (6.1.1) reduces to \( -(\alpha \beta/C_p) \partial I(r, t)/\partial t \), where \( I \) is the laser intensity, \( r \) is the radial coordinate, and \( \alpha \) is the absorption coefficient.

Sound production by a cylindrically symmetrical laser beam exciting an optically thin liquid has been discussed by Bechuck et al. \([6.3]\), Lai and Young \([6.4]\), Heritier \([6.5]\) and Brueck et al. \([6.6]\), and has been studied experimentally by Sullivan and Tam \([6.7]\), and Sigrist and Kneubuhl \([6.8]\). It should be noted that the calculations for liquids given by these authors apply equally to gases (unless unusually low pressures are employed) except that the contribution from electrostriction can be expected to be comparatively small. The formulation of the problem by Heritier will be outlined here, where a Gaussian heating function of the form

\[
 H(r, t) = \frac{2\alpha E_0}{\pi^{3/2} w_0^2 \tau_1} \exp \left( -\frac{2r^2}{w_0^2} - \frac{t^2}{\tau_1^2} \right) \tag{6.1.3}
\]

is considered. Here, \( E_0 \) is the total energy in the pulse, \( w_0 \) is the beam radius, and \( \tau_1 \) is the pulse width; that is, the e\(^{-1}\) points are defined as \( \tau_1 \) and \( w_0/\sqrt{2} \). To solve the wave equation for the pressure as given by (6.1.1) the time-dependent quantities are written in terms of their Fourier transforms:

\[
 p(r, t) = \int_{-\infty}^{\infty} d\omega \ p(r, \omega) e^{-i\omega t},
 p(r, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ p(r, t) e^{i\omega t}. \tag{6.1.4}
\]