Photoacoustic Spectroscopy

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Introduction

- The photoacoustic (PA) or optoacoustic (OA) effect, i.e. the generation of acoustic waves due to the absorption of modulated electromagnetic waves, is an old effect, discovered by Bell in 1880.

- This effect is weak; only a very small fraction (<1ppm) of the absorbed optical energy is converted into acoustic energy.
Kreuzer (1971) reported that an ultra low gas concentration can be detected by OA using an infrared laser beam as a light source.

A sensitivity limit of a concentration of $10^{-8}$ of methane in nitrogen was demonstrated, and a limit as low as $10^{-13}$ could be expected with an improved light source.
Fig. 1. Block diagram of some factors to be considered in the theory of OA detection.
Theory

- First step: Optical absorption, which results in the production of excited states.

- Let’s take a two-level system, which involves the ground state and the excited state (N and N’)

- N’ can be calculated using the rate equation as:

\[
\frac{dN}{dt} = \frac{\left(N - N'\right)}{R} - \frac{\left(N + N'\right)}{A_n} + \frac{\left(N + N'\right)}{A_r} - \frac{\left(N + N'\right)}{\Phi \sigma}.
\]

Where \(A_r\) is the radiative decay rate of the excited state, \(A_n\) is the non-radiative decay rate due to collisions of the excited state, and \(R\) is the excitation rate due to the light beam of flux \(\Phi\) photons per \(\text{cm}^2 \text{ sec}^{-1}\) with an absorption cross section \(\sigma\) \(\text{cm}^2\).
In many cases, the modulation frequency of the light is slow (\(~\text{kHz or less}\) compared to the excited-state decay rate.

Furthermore, the light intensity is usually weak enough so that \((N \gg \text{N}^{-})\) and the stimulated emission from the excited state can be neglected. (slow modulation and weak light)

Where the lifetime of the excited state...
Heat production rate (H) due to the excited-state density $N'$ (which depends on position $\mathbf{r}$ and time $t$, because $\Phi$ is a function of $\mathbf{r}$ and $t$) is given by:

\[ ... 3 \]

Where $E'$ is the average thermal energy released due to a non-radiative de-excitation collision of the excited state.
If the deexcitation collision results in converting the excited state to the ground state, then the deexcitation energy is simply the energy of the excited state with respect to the ground state.

Equation 3 states that heat source term for the OA signal is proportional to the product of molecular density ($N$), photon absorption rate $\Phi \sigma$, probability for nonradiative relaxation of the optically excited state $\tau A_n$, and the heat energy released per deexcitation $E'$. 
Equation 3 is applicable only when the modulation frequency of the light is slow compared to the excited-state decay rate.

If this condition is not met, we cannot put $dN/dt$. Instead of that, we may rewrite equation 1 as:

where we have again assumed the absence of optical saturation, i.e., we have assumed $N' \ll N$ or $R \ll \tau^{-1}$. The incident light flux is assumed to be sinusoidally modulated, i.e.,
Theory cont..

- Where only the real part has physical meaning
- We may drop the constant in equation 5 since we are interested only in the modulated heat source which generates a corresponding OA signal.
- The solution of equations 4 and 5 is:

where
Theory cont..

- $\Psi$ is the phase lag of the modulation of the excited-state density compared to the optical excitation, and is large when the excited state decays more slowly than the modulated rate of the light intensity.

- Note that equation 6 reduces to equation 2 in the limit when $\omega M$.

- The heat generation term $H$ corresponding to equation 6 is again given by equation 3.
As seen in the schematics, the next step in the theory is the generation of acoustic waves by the heat source $H(r,t)$ of equation 3.

Inhomogeneous wave equation relating the acoustic pressure $p$ and the heat source $H$:

\[
\ldots 7
\]

After Morse and Ingard (1968)

Where $c$ is the velocity of sound and is the ratio of specific heats of the gas; all dissipative terms have been neglected.
Equation 7 is usually solved for the sinusoidal modulation case by expressing the Fourier transform of $p$ in terms of “normal acoustic modes” $p_j$ which satisfy the appropriate boundary conditions. Thus

$$... 8$$

with the normal mode $p_j$ being solutions of the homogeneous wave equation, i.e.,
Theory cont..

- $p_j$ must be chosen to satisfy the boundary condition that the gradient of $p$ normal to the cell wall vanish at the wall, since acoustic velocity is proportional to the gradient of $p$ and must vanish at the wall.

- The resultant orthonormal modes in the cylindrical geometry are given by:

\[
\text{after Morse and Ingard (1968) ... 9}
\]

with a corresponding angular frequency $\omega_j$ given by

\[
\text{... 10}
\]
Here $g_j$ is a normalization constant; $L$ is the length and $R_0$ the radius of the gas cell; $(r, \varphi, z)$ are the cylindrical coordinates of a spatial point; $k$, $m$, and $n$ are the longitudinal, azimuthal, and radial mode numbers; $J_m$ is a Bessel function; and $\alpha_{mn}$ is the $n$th solution of the equation $dJ_m/dr = 0$ at $r = R_0$.

The condition of vanishing pressure gradient at the cell wall requires that the acoustic pressure $p(r, \omega)$ be expressed as linear combinations of eigenmodes $p_j$ of the form of equation 9 for a cylindrical geometry.
Solving the expansion coefficients $A_j(\omega)$

Fourier transform of equation 7 is:

Substituting equation 8 in the above equation and using the orthonormal conditions for the eigenfunctions $p_j$, we may solve for $A_j$ as:
Here $V_0$ is the cell volume, $Q_j$ is the quality factor for the acoustic mode $P_j$ ($P_j^*$ is the complex conjugate of $p_j$), and the integral is over the volume of the cell.

$Q_j$ accounts for the mode damping and avoid the physically unreasonable situation of $A_j \rightarrow 0$ as $\omega_j$

Equation 12 may be further simplified for the case $H$ being given by equations 2 and 3. In this case

Here we have lumped the space- and time-independent coefficients of $\Phi_0(r)$ together as the coefficient $q$. 
We also assumed that the light beam is Gaussian, i.e.,

\[
\text{where } a \text{ is the beam radius; beam propagates along the axis of cell so that only eigenmodes are of the form of equation}
\]

With an eigenfrequency \( \omega_j \) given by

Special case: Beam along the axis of cylinder OA cell in weak absorption limit, and only Normal modes can be excited by the heat source, i.e., we need only the radial normal modes.
The amplitude of the lowest-order radial pressure mode \((j=1)\) is then given by equation 12 as:

\[
\text{Where,} \quad g_1 = \text{normalization factor for} \quad \text{, and} \quad L = \text{cell length}
\]

and we have used
Close to resonance ($\omega = \omega_1 + \delta$; $\delta$ being small), this equation reduces to:

$$ \cdots 13 $$

This equation contains the basic physics of the operation of a resonant OA cell.

Resonant enhancement of the amplitude of the radial pressure $j=1$ is obtained when the fractional detuning from resonance $\delta$ is less than $(2Q_1)^{-1}$.

In general, larger acoustic amplitude is obtained for larger specific heat ratio $\gamma$, larger light power absorbed $q\Phi_0 L$, smaller beam excitation radius $a$, and smaller cell volume $V_0$. 

Theoretical Hydrodynamics
This equation is valid for near resonance to the lowest radial mode. For the opposite case of far off-resonance (i.e. non resonant OA cell), then:

\[ \omega \ll \omega_1 \], i.e. the light beam modulation frequency being much less than the lowest-radial-mode resonance frequency

In this nonresonant mode operation (common in OA), the acoustic amplitude lags behind the beam modulation by 90°.
Theory cont..

Fig. 2. Schematic of the OA signal \( p(t) \) (full line) and the incident photon flux \( \Phi(t) \) (dotted line) for (a) modulated cw excitation (nonresonant) case, and (b) pulsed excitation case. [Part (b) is drawn after Rosengren (1975).]
Final step of the theory of OA is the detection, which is frequently done with a microphone.

If the microphone has a known frequency response, then all the various components $A_j$ in equation 12 with frequencies $\omega_j$ within in the microphone bandwidth will be detected, and suitable frequency analysis of the microphone signal should give the various $A_j$'s.
In case of pulsed OA excitation, boundary conditions are frequently unimportant when short-duration light pulses are used because the time needed for the acoustic wave to reach the OA cell well is roughly 30 microseconds, which’s much longer than the light pulse duration and much longer than decay times of excited states in most gases.

Thus, interference of the generated acoustic wave and the reflected acoustic waves generally do not occur in contrast to the CW modulated case.

However, Pulsed OA generation does produce a “ringing” acoustic signal due to multiple reflections in the gas cell.
The net heat released up to time $t$ is:

$$W$$

where $W$ is the total number of photons absorbed

The pressure increase of the irradiated column of gas of volume $V$ by using the ideal gas law:

$$P = \frac{nRT}{V}$$

Where $R$ is the universal gas constant, $M$ is the molecular weight, and $C_v$ is the specific heat per unit mass at constant volume.
The time dependence of $p(t)$ for the pulsed OA signal is indicated in slide 22(b) for the case of short optical pulse duration and long thermal diffusion time $\tau_D$, given by

$$\tau_D = \frac{a^2}{L}$$

where $a$ is the beam radius and $D$ is the thermal diffusivity of the gas.

The initial rise in $p(t)$ depends on the lifetime of the excited state, while the final slow decrease of $p(t)$ back to zero depends on the thermal decay time constant $\tau_D$. 
Instrumentation for OA Studies of Gases

Fig. 3. Schematic of a general OA detection experiment.
Instrumentation for OA Studies of Gases

Instruments:

- Light source
- OA cell with transducer
- A means of modulating the light source (e.g., pulsing a laser or using a chopper), or modulating the sample absorption (e.g., using a modulated electric field for Stark modulation of the absorption)
Instrumentation: Light Source

Two general classes:

- **Lamps, filament lamps, and glow bars**
  - Inexpensive, usually compact and reliable, and cover broad spectral ranges from the UV to the far IR.
  - Low spectral brightness, incapability of fast modulation or switching, and necessity of an external spectral selection element like a monochromator.
Instrumentation: Light Source

- **Lasers**
  - High spectral brightness and collimation, can be readily modulated by extracavity or by intracavity means, and are of narrow spectral linewidth.
  - Expensive and limited tuning range.
OA cells for gases

Fig. 4. Schematic drawings of several types of OA cells for measurements in gases, used in the literature.
Resonances in OA cells

Fig. 5. Various types of resonances in OA cells.
Applications

- Measurement of weak absorption lines
  \[ (\sim 10^{-10}\text{cm}^{-1}/\text{cell length} \sim 10\text{cm} \text{ (Patel et al 1977)}) \]
- High sensitivity trace detection (SFRL)
- Absorption of excited states
- Chemically reactive gases
- Raman-Gain Spectroscopy (PARS) [non-linear]
PA Spectroscopy in Condensed Matter

- Two methods:
  1. The Gas-Coupling Method
  2. The Direct Coupling Method
Gas-Coupling Method

- Use of gas-phase microphone for detecting PA signals in condensed matter
- PA signal was generated by sinusoidally modulated CW light beam incident on the condensed sample, and the periodic heating of the gas at the irradiated surface of the sample generated the acoustic wave, which was detected by a gas-phase microphone.
Fig. 10. Block diagram to explain the method of PA detection in condensed matter using gas coupling.
Gas-Coupling Method

- The periodic heating of the sample occurs in the “absorption length” $\mu_\alpha$ of the sample.
- But only the heat within a diffusion length $\mu_s$ from the interface can communicate with the gas and heat up a layer of gas of length $\mu_g$ (diffusion length in gas) which expands periodically, producing acoustic waves.

$D_s$ and $D_g$ are the thermal diffusivities in the sample and in the gas, respectively and $f$ is the modulation frequency of the light beam.
Gas-Coupling Method

A light beam of radius $r$ striking a flat opaque surface of radius $R$. 

Fig. 11. Simplified PA signal generation theory for optically opaque sample due to modulated cw light beam and microphone detection. [After Tam and Wong (1980).]
The heat generated in the thin absorption layer of thickness is mainly conducted into the condensed sample (heat conduction into the gas is much smaller); the heat conduction equation is:

\[ \theta_0 \] is the amplitude of the surface temperature modulation and \( I_0 \) is the modulated light absorbed

\( \theta_0 \) is coupled to an active gas volume \( V_{\text{act}} \) near the sample surface, given by:

\[ V_{\text{act}} \leq \frac{\mu_g}{\mu_g} \quad \text{for} \ l_g > \mu_g \]

\[ V_{\text{act}} \leq \frac{2\mu_g}{\mu_g} \quad \text{for} \ l_g < \mu_g \]
Gas-Coupling Method

- Using the ideal gas law, we obtain the amplitude $\delta V$ of the volume change of $V_{\text{act}}$:

$$
\delta V = \frac{RT_0}{V_0} \ln \left( \frac{T}{T_0} \right)
$$

($T_0$ is the ambient temperature)

- The corresponding pressure change $\delta P$ is obtained by considering an adiabatic expansion of an ideal gas:

$$
\delta P = \frac{\gamma P_0 V_0}{R} \left( \frac{T}{T_0} \right)^{\gamma - 1}
$$

Where $V$ is the total PA cell volume given by:
Gas-Coupling Method

- Here $V_{res}$ is the residual cell volume for $l_g=0$, and can be due to the dead space in front of the microphone. Finally, we have:

$$V_{res} = V_{g} - V_{g \text{ - res}}$$

where

- Optimum $l_g$ exists, which’s found to be $l_g \approx 1.8\mu l$.
Gas-Coupling Method

Fig. 12. Simple PA cell with flat microphone. A mirror at 45° to the vertical for directing a horizontal light beam onto the sample is sometimes attached to the upper part of the cell. [After Rosencwaig (1977).]
Direct-Coupling Method

Problems with Gas-Coupling led to the invention of Direct-Coupling method (microphone signal due to acoustic vibration).

It involves the insertion or attachment of a transducer (usually piezoelectric) into or onto the sample without the intervention of a gas medium.

Thus, the serious acoustic impedance mismatch from condensed matter to gas can be avoided.
Direct-Coupling Method

Two general types of PA excitation are:

1. The use of a **chopped or modulated CW** excitation beam when the detected PA signal depends on the boundary conditions.

2. The use of a **pulsed** excitation beam when the boundary conditions frequently have no effect on the detected optoacoustic signal, especially if short-duration pulses (<1 μs) at low repetition rate (~10 Hz) are used.
Fig. 19. Experimental arrangement to perform pulsed OA spectroscopy for measuring weak absorptions in liquids. [After Tam et al. (1979).]
Direct-Coupling Method

Fig. 20. Cross section of the homemade piezoelectric transducer utilizing a lead zirconate titanate cylinder (LTZ-2 or PZT-5A). [After Tam and Patel (1980).]
Substance

- PA or OA spectroscopy is based on OA effect.
- Generation of acoustic waves due to the absorption of a modulated EM wave.
- Can be done to analyze gas and condense matter.
- Very useful and can be used efficiently for trace detection, depth profile studies, etc. !!
Discussion

( Don’t Ask, Can’t Tell )
References

Thank You