Photoacoustic spectroscopy of solids

The generation of sound from a periodically illuminated solid, an effect first discovered in 1881, is now being used to study the properties of materials not accessible to optical spectroscopy.

Allan Rosencwaig

One of the most effective means for studying the properties of matter nondestructively is to observe how photons interact with it; that is, by optical spectroscopy. The two most common techniques in the optical region are absorption and reflection spectroscopy. But many organic and inorganic materials, such as powders, amorphous compounds, smears, gels and oils, can not be readily studied by either of these two techniques. Methods involving diffuse or attenuated total reflectance permit the study of some of these materials, but they possess severe drawbacks.

A new technique recently developed at Bell Laboratories for the investigation of solid and semisolid matter[1] overcomes many of these drawbacks. In this new technique, called "photoacoustic spectroscopy," modulated light absorbed by a sample is converted into sound, which is then detected by a microphone. Its principal advantage is that it permits us to obtain spectra similar to those from optical-absorption spectroscopy on any type of solid or semisolid material. Scattered light, which presents such a severe problem when we deal with many solid and semisolid materials by conventional techniques, presents no difficulties in photoacoustic spectroscopy because only the absorbed light is converted into sound. I have found that photoacoustic spectroscopy can be a very useful tool for research and analysis, not only in physics and chemistry but also in biology and medicine.[2–6] Before examining these applications, let us briefly look at the history of photoacoustic spectroscopy and its theory.

What causes the effect?

Photoacoustic spectroscopy has its historical roots in the 1880's when Alexander Graham Bell, John Tyndall and Wilhelm Röntgen first studied[7] the so-called "opto-acoustic effect." This effect occurs when a gas in an enclosed cell is illuminated with periodically interrupted light. Energy absorbed by the gas is converted into kinetic energy of the gas molecules, giving rise to pressure fluctuations within the cell. These pressure fluctuations were detected in 1881 as audible sound through a hearing tube.

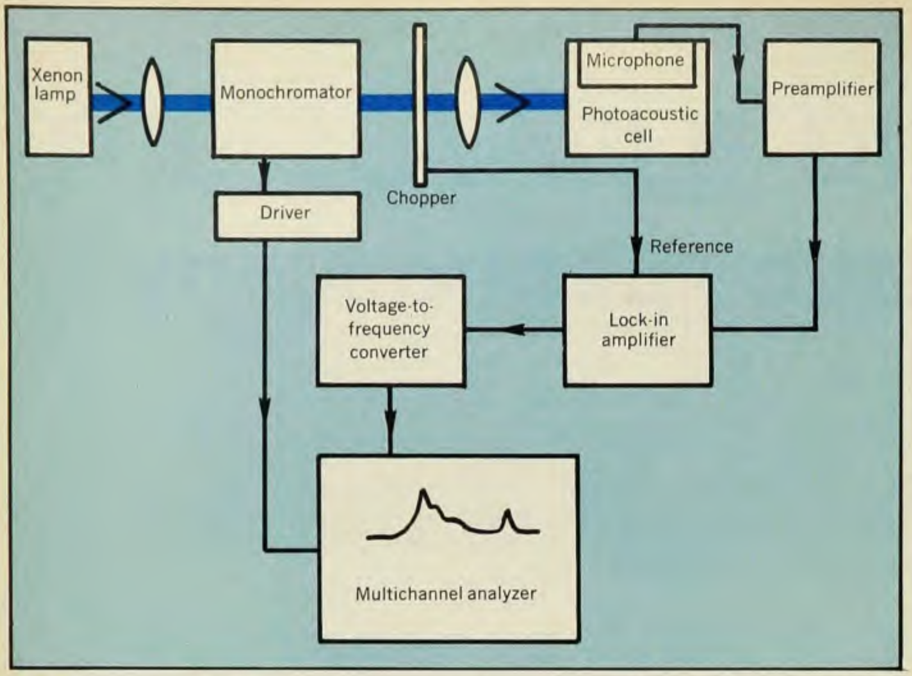
The opto-acoustic effect, here called the photoacoustic effect (to remove confusion with the "acousto-optic effect," wherein a laser beam interacts with acoustic waves in a crystal) has been used fairly extensively since then, primarily for gas analysis. More recently it was used by Lloyd Kreuzer and Kumar Patel[8] to study gaseous pollutants and by Mel Robin and his coworkers[9] to perform studies on photochemical and kinetic effects in gases. Although the photoacoustic technique has been thoroughly developed for gases, the analogous effects in solids and liquids were apparently not studied until recently, despite initial experiments along these lines by Bell in 1881.

In photoacoustic spectroscopy of solids, the sample is placed inside a specially designed closed cell containing air (or other suitable gas) and a sensitive microphone. The solid is then illuminated with chopped monochromatic light, as figure 1 indicates.

Bell had attributed the presence of an acoustic signal from a solid to a cyclic process in which gases are driven off, and readsorbed onto, the surface in response to the cyclical heating and cooling effect of the chopped light. However, I have found, from experiments in which I thoroughly evacuated the photoacoustic cell and then refilled it with nonadsorbing noble gases as well as from experiments with two-dimensional solids and other systems with weak surface-adsorption properties, that adsorbed gases generally do not play a significant role in the production of the acoustic signal. I have also shown that the cyclical expansion and contraction of the solid cannot be the major source of the signal. I have therefore concluded from these experiments along with the theory outlined below that the primary source of the acoustic signal arises instead from the periodic *heat flow* from the solid to the surrounding gas, as the solid is cyclically heated by the absorption of the chopped light. This conclusion was independently arrived at by John Parker at Johns Hopkins University.

Nonradiative de-excitation processes convert part or all of the light absorbed by the solid into heat. The periodic flow of this heat into the gas of the cell produces pressure fluctuations in it; this is how the sound originates. In an experiment, these fluctuations are then detected by the microphone. The analog signal from the microphone is recorded as a function of the wavelength of the incident light. Suitable normalization procedures remove the spectral structures of the light source, the monochromator and so on.

Allan Rosencwaig is a member of the technical staff of Bell Laboratories, Murray Hill, N.J.



Block diagram of a single-beam photoacoustic spectrometer with digital data acquisition. Because of the photoacoustic effect, the solid in the cell emits sound when it is illuminated with chopped monochromatic light. The resulting frequency spectrum, displayed on the multichannel analyzer, has a wide variety of potentially useful applications in physics, chemistry, biology and medicine. Figure 1

Because the magnitude of the acoustic signal in the photoacoustic cell is proportional to the amount of heat emanating from the solid absorber, there is a close correspondence between the strength of the acoustic signal and the amount of light absorbed by the sample. The quantitative analysis of the photoacoustic process in solids, derived in collaboration with Allen Gersho,[10] outlined below shows that the magnitude and phase of the acoustic signal also depend on the thermal properties of the sample and of the gas in the cell, and on the chopping frequency. In spite of a rather complicated dependence, the photoacoustic spectrum turns out to correspond closely to the optical absorption spectrum of the sample, provided that the nonradiative processes dominate in the dissipation of the absorbed light energy.

Theory

In the analysis of the production of the acoustic pressure from periodic heat flow, let us consider a simple cylindrical cell such as the one in figure 2. Let us assume for the sake of simplicity that the cell has dimensions small compared to the wavelength of the acoustic wave. The sample, assumed to be a disc of thickness l, is placed against a backing material and the rest of the cell is filled with a gas such as air. The sample is illuminated with monochromatic light chopped so as to produce what is essentially a sinusoidal intensity modulation. The temperature in the sample, $\varphi_s(x,t)$, can then be evaluated from the following equation for thermal diffusion

$$\frac{\partial^2\varphi_s}{\partial x^2} = \frac{1}{\alpha_s}\frac{\partial\varphi_s}{\partial t} - Ae^{\beta x}\,(1 + e^{i\omega t})$$

where α_s is the thermal diffusivity of the sample (equal to $k_s/\rho_s C_s$; k_s, ρ_s and C_s being respectively the thermal conductivity, the density and the specific heat of the sample) and $A = \beta I_0\eta/2\,k_s$, with β the optical absorption coefficient of the sample, I_0 the light flux, and η the efficiency with which the absorbed light energy is converted into localized heat by the nonradiative de-excitation processes. The chopping freqency is $\omega/2\pi$. Note that the sample is located between $x = -l$ and $x = 0$ and that light enters on the right and is attenuated toward the left.

The general solution for equation 1 is given by

$$\varphi_s(x,t) = a_1 + a_2x - \frac{1}{\beta^2}e^{\beta x} + \varphi_1(x)\,e^{i\omega t}$$

with

$$\varphi_1(x) = Ue^{\lambda_s x} + Ve^{-\lambda_s x} - \left(\frac{A}{\beta^2 - \lambda_s{}^2}\right)e^{\beta x}$$

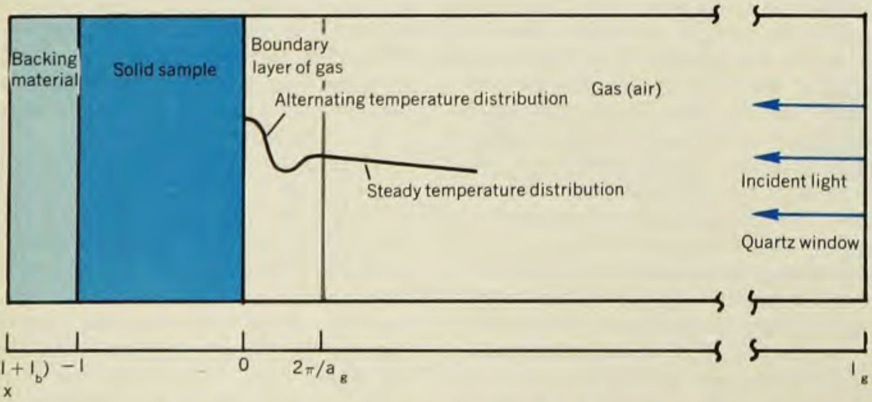
where $\lambda_s = (1 + i)a_s$ and $1/a_s$, the thermal-diffusion length in the sample, is $(2\alpha_s/\omega)^{1/2}$. The parameters a_1, a_2, U and V can be determined by making use of the boundary conditions at the sample-gas interface ($x = 0$) and the sample-backing interface ($x = -l$). The boundary conditions used are the continuity of temperature and of heat flow.

Once the boundary condition equations are solved, the coefficients a_1, a_2, U and V, and thus the sample temperature $\varphi_s(x,t)$, can be derived in terms of the optical, thermal and geometrical parameters of the sample, the gas and the backing material. The temperature of the gas in the cell, $\varphi_g(x,t)$, can in turn be determined from the temperature at the surface of the sample, $\varphi_s(0,t)$, and the ambient temperature at the cell walls. When convection effects can be neglected, the periodic temperature fluctuation produced in the gas by the varying temperature at the sample surface falls off exponentially in magnitude with distance from this surface, as depicted in figure 2. For all practical purposes, the temperature oscillation is limited to a boundary layer of gas of thickness about $2\pi/a_g$, where $1/a_g = (2\alpha_g/\omega)^{1/2}$ is the thermal diffusion length in the gas. For air at room temperature and pressure, this boundary layer is about 1 mm thick when ω = 1000 rad/sec.

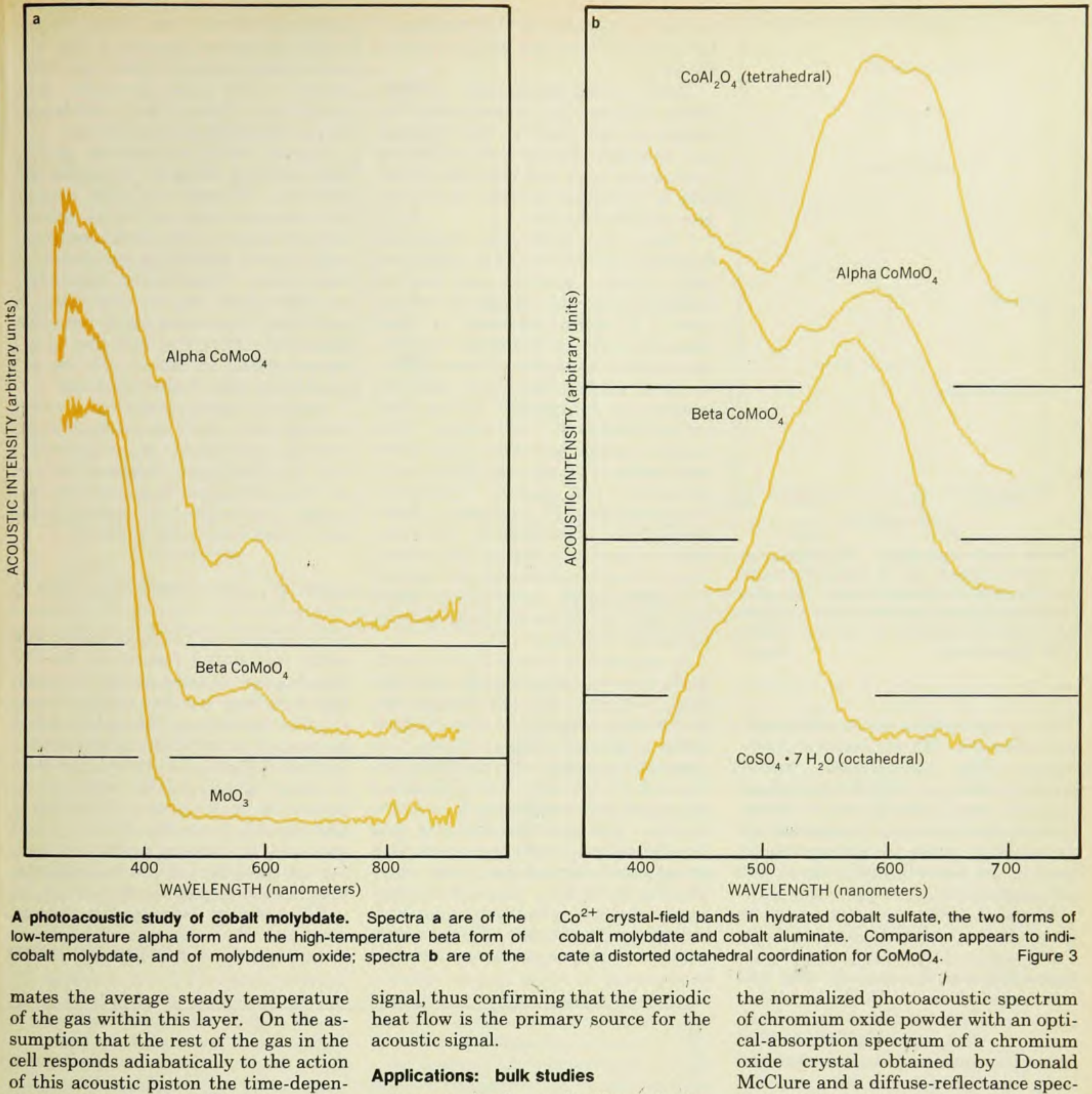
We can approximate the pressure effect of the periodic temperature variation within this boundary layer by considering it as an acoustic piston. The displacement of this piston is given by

$$x(t) = \frac{2\pi}{a_g}\frac{\langle\varphi_g(t)\rangle}{\varphi_0(0)}$$

where $\langle\varphi_g(t)\rangle$ represents the periodic temperature averaged over the boundary layer and $\varphi_0(0)$, the steady temperature of the sample at x = 0, approxi-



Cross-sectional view of a simple cylindrical photoacoustic cell, showing the locations of the backing material and the solid sample. The colored curve shows the temperature distribution in the gas, which alternates within the boundary layer and shows a slight steady decrease outside of it. Some dimensions defined in the text are indicated on the x axis. Figure 2



A photoacoustic study of cobalt molybdate. Spectra **a** are of the low-temperature alpha form and the high-temperature beta form of cobalt molybdate, and of molybdenum oxide; spectra **b** are of the Co^{2+} crystal-field bands in hydrated cobalt sulfate, the two forms of cobalt molybdate and cobalt aluminate. Comparison appears to indicate a distorted octahedral coordination for CoMoO$_4$. Figure 3

mates the average steady temperature of the gas within this layer. On the assumption that the rest of the gas in the cell responds adiabatically to the action of this acoustic piston the time-dependent pressure in the cell is

$$p(t) = \frac{\gamma P_0}{l_g} x(t)$$

where γ is the ratio of the specific heats of the gas, p_0 the ambient pressure and l_g the length of the gas column.

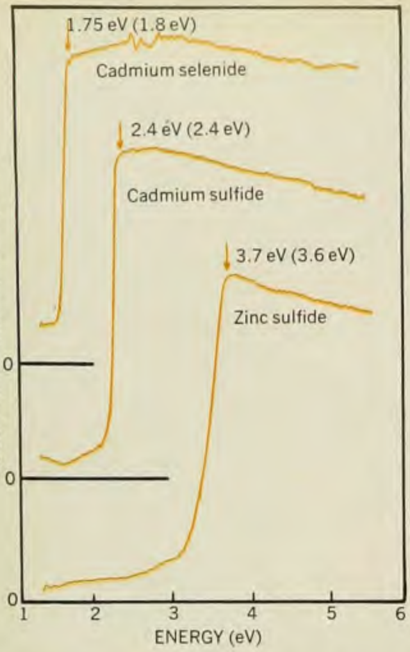
The final expression for the temperature variation is fairly complicated, involving not only the optical parameters of the sample itself but also thermal and geometrical parameters of sample, gas and backing material. Nevertheless, the theory shows that a photoacoustic spectrum will provide information, through both magnitude and phase, about the optical-absorption characteristics of the sample. This theory has been found to agree quantitatively with experimental data on the magnitude and phase of the acoustic signal, thus confirming that the periodic heat flow is the primary source for the acoustic signal.

Applications: bulk studies

In general, the applications of photoacoustic spectroscopy can be divided into three main areas—bulk studies, surface studies and de-excitation studies. When the surface of a solid material is not highly reflective, photoacoustic spectroscopy will provide optical data about the bulk material itself. The photoacoustic technique can thus be used to study insulator, semiconductor and even metallic systems that cannot be studied readily by conventional absorption or reflection techniques. This includes substances that are in the form of powders, are amorphous or are for some reason difficult to prepare for reflection studies.

In the case of insulators, photoacoustic spectra give direct information about the optical-absorption bands of the material. For example, I compared the normalized photoacoustic spectrum of chromium oxide powder with an optical-absorption spectrum of a chromium oxide crystal obtained by Donald McClure and a diffuse-reflectance spectrum of the powder obtained by S. P. Tandon and J. P. Gupta. The two crystal field bands of the Cr^{3+} ion at 600 and 460 nm in the photoacoustic spectrum of the powder are almost as clearly resolved as in the absorption spectrum of the crystal, and they are much better resolved than in the diffuse-reflectance spectrum.

Figure 3 shows data obtained from an experiment on another inorganic insulator system, cobalt molybdate. This experiment was performed in hope of obtaining further understanding of the catalytic action of CoMoO$_4$ supported on alumina[11] in various reactions such as removing sulfur from oil while hydrogenating it. Both the high-temperature phase, beta CoMoO$_4$, and the low-temperature phase, alpha CoMoO$_4$, are available as fine precipitates only.



Theory *versus* experiment. The photoacoustic spectra shown are of three direct-band semiconductors in powder form. The numbers in parentheses give the literature values for the optical band gaps (in electron volts) at room temperature. Figure 4

Their optical spectra are thus not readily obtainable by conventional techniques. The photoacoustic spectra shown in part a of this figure indicate that the beta $CoMoO_4$ has a charge-transfer band similar to that seen in the parent MoO_3, while the charge-transfer band in the alpha $CoMoO_4$ has shifted noticeably to lower energy.

Part b of figure 3 examines in more detail the crystal-field bands of the Co^{2+} ions in $CoSO_4{\cdot}7H_2O$ (which has octahedral coordination) in the beta and alpha phases of $CoMoO_4$, and in $CoAl_2O_4$ (which has tetrahedral coordination). Comparison of these photoacoustic spectra indicates that the Co^{2+} ions in both the beta and the alpha phases of cobalt molybdate are in a distorted octahedral coordination, and that there is no significant change in the d-electron configuration of the Co^{2+} ion between the two phases. However, figure 3a indicates that the two phases of $CoMoO_4$ may have different catalytic properties because of the significant difference in the charge-transfer band between them. This study is being continued with the photoacoustic technique.

In the case of semiconductors, both direct transitions and those assisted by phonons can be observed. Figure 4 shows the results of a study of three semiconductors of the direct band-transition type. They are all in powder form. The band edges, as measured by the positions of the knees in the photoacoustic spectra agree very well with the values recorded in the literature.[12] In the figure these are given in parentheses.

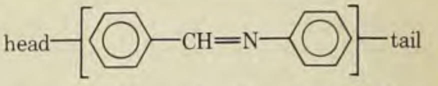
These room-temperature experiments indicate that photoacoustic experiments performed at low temperature and high resolution will allow one to study excitonic and other fine structure in crystalline, powder and amorphous semiconductors.

I have also found that interband transitions can be studied in highly metallic systems, provided that specular reflection from the surface is not too great. A major advantage of photoacoustic over conventional reflection spectroscopy in studies of semiconductors and metals is that highly reflecting surfaces are not needed—in fact, they are undesirable for bulk studies. This is a great advantage for the study of the new classes of organic and glassy semiconductors and metals. These are often available only in powder or amorphous form. Furthermore, the ultraclean surfaces so necessary for conventional reflection studies are not needed for photoacoustic spectroscopy; hence the use of elaborate high-vacuum equipment is avoided.

An example of results from a recent study on one-dimensional metallic systems, performed in collaboration with Al Ginsberg and Jeff Koepke, is illustrated in figure 5. This shows the photoacoustic spectrum obtained from the linear-chain conductor $K_2Ir_2(CO)_4Cl_5$, a compound now available only as a fine powder. The spectrum indicates that the delocalized conduction band is a strong broad infrared band that drops off in the visible. The lower-wavelength region is dominated by localized iridium-ion transitions. This example shows that photoacoustic spectroscopy readily allows us to study the UV and visible absorption spectra of these unusual compounds and obtain new information about their electronic band structures. These are of considerable current interest and controversy.

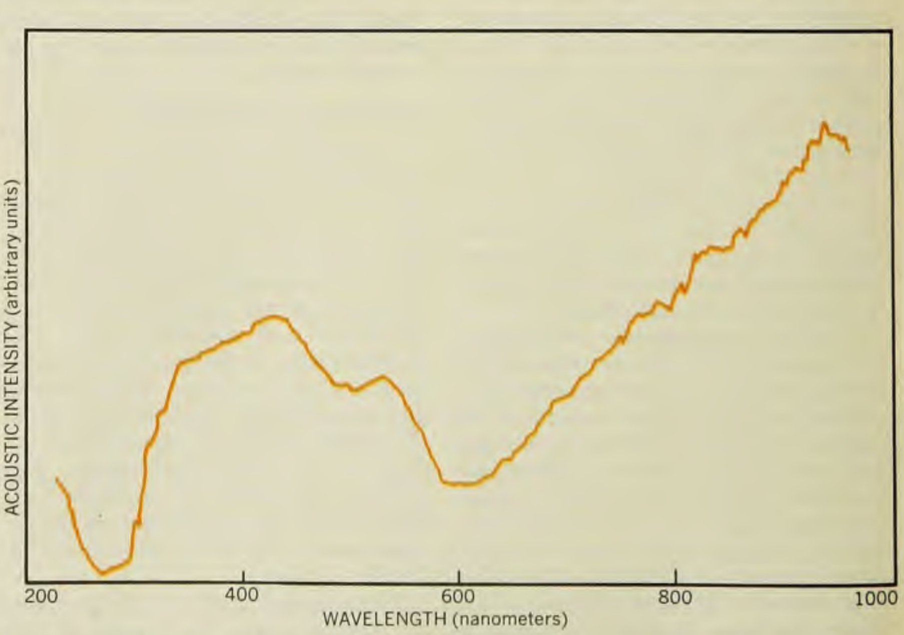
Organic liquid crystals are also of great interest, both to physicists and chemists. Because the solid, smectic and nematic states of liquid crystals strongly scatter light, optical spectroscopy cannot readily be performed on these states. Nevertheless, optical data on these states may be very useful in providing information about the intermolecular interactions that play so important a role in determining the unusual properties of these materials.

Figure 6a shows data from a recent photoacoustic study of a class of liquid crystals, performed in collaboration with Pat Cladis and Ghislaine Pasteur. All the members of this class are composed of molecules with essentially the same benzylidene aniline center

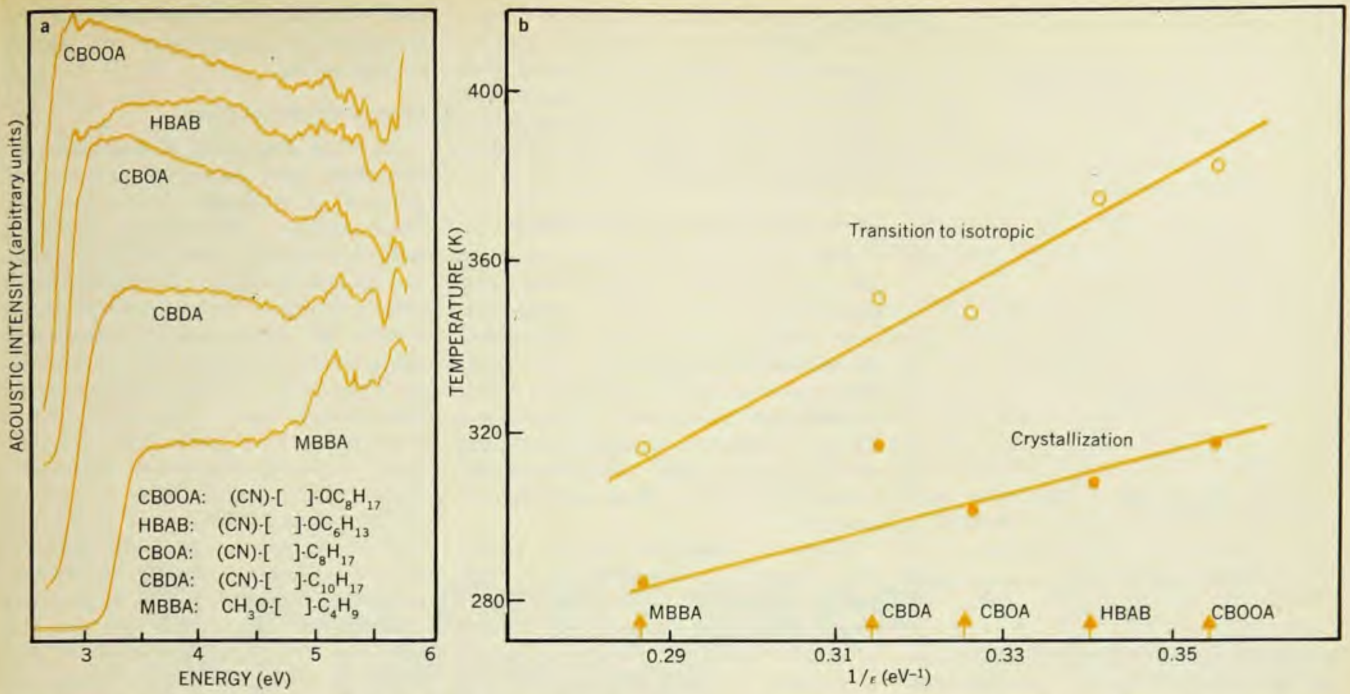


but with different heads and tails. As a result the general features of the UV photoacoustic spectra are quite similar. However, there is a clear shift in the position of the primary absorption edge as we proceed from MBBA, which has the formula CH_3O-[ ]-C_4H_9 to CBOOA, which is (CN)-[ ]-OC_8H_{17}; the brackets denote the center above. This shift is undoubtedly due to the different heads and tails, and thus is probably a measure of the different intermolecular interactions in these crystals.

A correlation between the spectral data and the intermolecular interactions is clearly seen in figure 6b. This



Photoacoustic spectrum of the linear-chain metal $K_2Ir_2(CO)_4Cl_5$. Even materials available only in powder form, such as this unusual compound, can be studied with this method. Figure 5



A study of five liquid crystals. Their photoacoustic spectra are shown in **a**; the brackets in the formulas refer to a benzylidene aniline center, the formula for which is given in the text. In **b** the temperatures at which these liquid crystals undergo their transitions to the isotropic form, and the crystal form, are plotted as functions of the reciprocal absorption-edge energies. Figure 6

shows the dependence of temperature at which these materials crystallize and that at which they go into the isotropic liquid state on the value $1/\epsilon$, where ϵ is the position of the primary absorption edge. This photoacoustic measurements of these liquid crystals can be used to obtain information about the intermolecular interactions in these crystals and therefore enhance our understanding of the unusual properties of these compounds.

Biology and medicine

I have also found that photoacoustic spectroscopy can be used to great advantage in biological studies, since many biological materials do not readily lend themselves to conventional spectroscopic techniques. The photoacoustic technique has been used in the study of several hemoproteins in their solid and smear form, including a study of hemoglobin in a smear of whole blood.[3]

The unique capabilities of photoacoustic spectroscopy enable it to be used to obtain optical absorption data on complex biological systems such as green leaves and other plant and animal matter. Because of these capabilities photoacoustic spectroscopy can be used as a quick and efficient screening tool in natural-products chemistry.[4] Using the photoacoustic spectrum obtained from only a few milligrams of a natural source such as a plant, animal or microorganism, Stan Hall of Rutgers University and I were able to determine the types and relative concentrations of those chemical byproducts of the metabolism of the organism that may have important physiological or bio-medicinal value. Such information can now be arrived at only after laborious extraction and analysis procedures, which often requires many grams of the natural source.

Photoacoustic spectroscopy can also play a potentially important role in medical studies. For example, I have used photoacoustic spectroscopy to monitor bacterial growth in cultures and on surfaces. It may also be possible to use the photoacoustic spectra of bacteria to identify them. Another possible medical use is in the study of animal and human tissues; both hard tissues such as teeth and bone, and soft tissues such as skin and muscle.

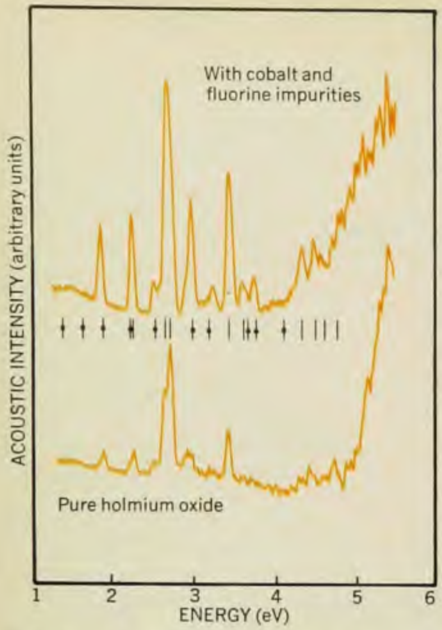
An example of an experiment on soft tissue is one performed in collaboration with Angelo Lamola in which we measured photoacoustic spectra of guinea pig epidermis that had been treated with a 2% solution of tetrachlorosalicylanilide (TCSA) in ethanol. This compound is known to be a highly effective antibacterial agent; unfortunately it also causes photosensitivity and other skin problems.[13] Why it has these side effects is not completely understood. We obtained a difference spectrum by subtracting the control spectrum of untreated guinea pig epidermis from the spectrum of the TCSA-treated skin. The difference spectrum is thus the spectrum of TCSA bound within the epidermis—a spectrum difficult, if not impossible, to obtain by any other technique. From this spectrum we can now establish the state of the TCSA compound *in situ* that is, when it is incorporated into the skin. Thus, we can learn more of its action on and in the skin under various conditions.

This example clearly illustrates the potential usefulness of photoacoustic spectroscopy in both research and clinical investigations of human tissue. Furthermore, it may well be that, with the photoacoustic technique, one might find a correlation between the spectral properties of soft tissues and their pathology and disease. The photoacoustic technique might then prove to be a valuable clinical tool for the early detection and diagnosis of various diseases such as cancer.

Surface studies

Photoacoustic spectroscopy can be used to great advantage in the study of adsorbed and chemisorbed molecular species and compounds on the surfaces of metals, semiconductors and even insulators. Such studies can be performed in any wavelength region in which the substrate is either nonabsorbing or highly reflecting. Under either of these conditions, photoacoustic experiments will give the optical absorption spectra of the adsorbed or chemisorbed compounds.

The first indication of the feasibility for using photoacoustic spectroscopy for surface studies came from an experiment with thin-layer chromatography.[5] This is a widely used, highly effective technique for the separation of mixtures into their constituent components, of considerable importance in chemistry, biology and medicine. The identification of the separated com-



Cobalt and fluorine impurities quench the natural fluorescence of the Ho^{3+} ions in the holmium oxide here studied by photoacoustic spectroscopy. The upper spectrum is of doped, and the lower spectrum of undoped, holmium oxide. The fluorescent levels of Ho^{3+} are marked with dots. Figure 7

pounds directly on the thin-layer-chromatography plates can, however, be a fairly difficult procedure—particularly if reagent chemistry is inappropriate. Conventional spectroscopic techniques are not suitable because of the opacity and light-scattering properties of the silica gel adsorbent on the plates. Hall and I found[5] that photoacoustic spectroscopy offers a simple and highly sensitive means for performing nondestructive compound identification directly on the chromatography plates.

In a photoacoustic experiment with benzylidene acetone spots of different concentrations, we were able to recognize features of the spectrum with no more than about one monolayer of the compound present in the spot. This experiment thus indicates the possibility that under certain conditions (low optical absorption or high reflectivity) of the substrate, the photoacoustic technique may well be sensitive enough to detect and identify a monolayer of adsorbed or chemisorbed compound. Some new experiments on both metallic and nonmetallic surfaces have shown that monolayer detectability is achievable.

The use of photoacoustic spectroscopy for such surface studies, particularly with high-resolution light sources such as tunable dye or infrared lasers, can lead to further understanding of oxidation and reduction processes and of catalytic activity on solid surfaces. Other possible subjects for study by photoacoustic spectroscopy include organic compounds and inorganic oxides purposely deposited on the surfaces of metals, semiconductors and polymers for passivation. Such studies would yield data about the structure, valence and complexing of the deposited compound, information that is now very difficult to obtain nondestructively.

De-excitation studies: fluorescence

The photoacoustic effect measures the nonradiative de-excitation processes that occur in a system after it has been optically excited (or in fact excited by any means whatsoever). The selective sensitivity of this technique to the nonradiative de-excitation channel can be used to great advantage in the study of fluorescent (and phosphorescent) materials as well as photosensitive substances.

When an optically excited energy level decays *via* fluorescence or phosphorescence, little or no sound is produced in the photoacoustic cell. This is illustrated in figure 7, where we consider the case of the fluorescent solid holmium oxide, Ho_2O_3. Several trivalent rare-earth ions including Ho^{3+} have strongly fluorescent energy levels; that is, levels that tend to de-excite through the emission of a photon rather than through phonon (heat) excitation. The upper photoacoustic spectrum in the figure is of some Ho_2O_3 powder containing cobalt and fluorine impurities. All the lines in this spectrum correspond to known Ho^{3+} energy levels; their positions are designated by the bars in the middle, with dots indicating which of the levels are normally fluorescent. In this material the fluorescence is highly quenched by the presence of the impurities, and thus both the fluorescent and the non-fluorescent lines appear in the photoacoustic spectrum. In the spectrum of pure Ho_2O_3 (lower curve), however, all the fluorescent levels have a greatly diminished relative intensity. That is because these levels are now de-exciting by the emission of a photon rather than through heating of the solid.

For fluorescent and phosphorescent solids, a combination of conventional fluorescence spectroscopy and photoacoustic spectroscopy will therefore provide data about both the radiative and nonradiative de-excitation processes. For the first time the complete de-excitation process can be readily studied within these compounds. By performing both fluorescence and photoacoustic spectroscopy as a function of temperature and compound composition, one can determine in a straightforward manner how these two variables affect the efficiencies and rates for the two de-excitation processes. Furthermore, since photoacoustic spectroscopy gives information on phase as well as amplitude, one may be able to study exciton processes (such as random walk and lifetimes) in these materials as functions of temperature and dopant concentration.

Photochemical studies

Another channel of de-excitation for absorbed light energy in some compounds is through photochemistry. Photoacoustic spectroscopy offers a unique tool for the study of photochemical process in solids. An illustration of this is shown in figure 8, which shows results of photoacoustic experiments performed in collaboration with Anthony Trozollo on the photosensitive material Cooper blue. This compound is colorless in the dark but reversibly turns to strong blue when exposed to light of short wavelength.

The bottom spectrum of figure 8 is the photoacoustic spectrum of dark-adapted Cooper blue. It shows substantial UV absorption but little visible absorption. The middle spectrum was obtained within minutes after the first but it is quite different, showing two strong absorption bands in the visible. These are the bands that give Cooper blue its blue color. These bands arise from photochemical change in which some of the photons absorbed in the short-wavelength region have broken a ring in the Cooper blue molecule and thus created a new compound. The

Photoacoustic spectra of Cooper blue. The photosensitive material was dark-adapted before the lower spectrum was made. The middle spectrum was run afterward, and then the upper spectrum, with only a few minutes separating the runs. Figure 8

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upper spectrum, run within minutes after the middle spectrum, shows further changes yet. These reflect further photochemical—and even photoinduced thermochemical—processes.

Photoacoustic spectroscopy not only allows us readily to see the effects of photochemistry but also to establish the activation spectrum for the photochemical process directly. This is done simply by comparing the photoacoustic spectrum with a conventional absorption spectrum. Information about the activation spectrum of photosensitive materials is at present quite difficult to obtain by other means. In addition we can obtain data from the phase measurements of the photoacoustic signal about photochemical reaction rates. These data even distinguish between true photochemical events and photoinduced thermochemical events. Photoacoustic studies on photosensitive materials can provide not only valuable basic information about the physical and chemical processes in these materials, but can also be of great benefit in the understanding of technologically important compounds such as the photoresist resins used in fabricating integrated circuits. The technique is also useful in the study of photoinduced physical and chemical changes in polymers, plastics and pigments.

Since the subject of photoacoustic spectroscopy is still in its formative stages, its potential can be expected to increase substantially as this new technique is expanded further into the infrared and ultraviolet regions of the spectrum.

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