The Opto-Acoustic Effect: Revival of an Old Technique for Molecular Spectroscopy

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Over 90 years ago, Alexander Graham Bell described qualitatively the results of a series of experiments which have gone virtually unnoticed by succeeding generations of molecular spectroscopists until the present.[1]

In his pioneering experiments, Bell focused undispersed sunlight onto a sample tube with a lens and, between the sample tube and the lens, placed a rotating slotted disk. If the light fell intermittently on a solid, liquid, or gas in the sample tube and was absorbed, then the observer witnessed a "sonorousness" through an attached listening tube (a short length of tubing connected at one end to the sample cell, with the other end placed in the observer's ear). The frequency of the emitted sound was just that at which the light was chopped.

The transformation of optic to acoustic energy is easy to see: the pulses of absorbed optical quanta are degraded in the sample to heat pulses, which in a gas express themselves as pressure pulses, *i.e.*, sound. In summarizing the sonorous effects produced in a variety of materials, Bell prophesied, "*I recognize the fact that the spectrophone must ever remain a mere adjunct to the spectroscope; but I anticipate that it has a wide and independent field of usefulness in the investigation of absorption-spectra in the ultra-red.*" Though the history of this effect for the last 90 years argues against Bell, we too share his optimism for the future.

At the time the opto-acoustic effect was first discovered, Tyndall[2] argued that it was due solely to the absorption of infrared radiation, but using a prism disperser, Bell successfully demonstrated the effect using visible and even ultraviolet radiation. Still, research in this area up to the present has been confined to the excitation of vibrational transitions in the infrared.

We are presently doing opto-acoustic spectroscopy using an updated version of Bell's concept (Figure 1). In our study, the light source is a 4200-W xenon lamp, the output of which is chopped at between 10 and 2000 Hz and passed through a 0.25-m grating monochromator fitted with a prism predisperser. The dispersed radiation (32 Å/mm) is incident upon a steel cell filled with the absorbing gas of interest and containing a foil-electret microphone.[3] A lock-in detector follows the microphone signal in phase and out of phase with the synchronous chopping signal as the wavelength is scanned from 10,000 to 2000 Å. Chemical resistance of the cell is excellent since all of its parts are either steel, quartz, Teflon, or gold.

Our interest in this technique springs directly from the recent work of Kreuzer, *et al.*,[4-6] who were able to detect very low concentrations of contaminants in a gas by tuning an infrared laser to a vibrational frequency of the contaminant and recording the microphonic signal resulting from the absorption. Used in this way, the device is simply the well-known infrared spectrophone ordinarily used to study vibrational relaxation rates,[7,8] transformed to a tool for analytical chemistry.

Though our interests are not in analytical chemistry, we were struck with the sensitivity of the technique. Kreuzer showed that with this simple microphone and phase-sensitive detection, the absorption of 10^{-9} W of optical power would give a signal-to-noise ratio of 1, with a factor of 100 or so improvement expected upon optimizing the microphone parameters. On the other hand, with a bandpass of 32 Å, the lamp-monochromator combination of Figure 1 will yield *ca.* 10^{-3} W at all wavelengths between 10,000 and 2100 Å. Thus the optical spectrophone

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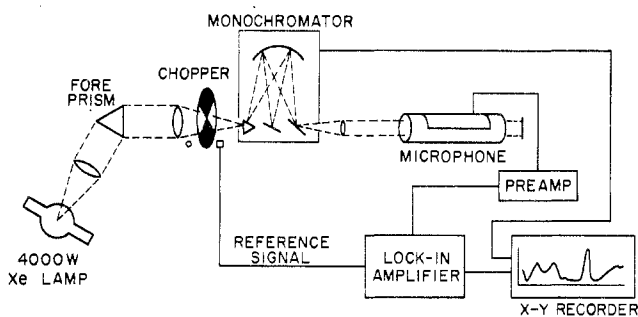(8) A. W. Read, *Advan. Mol. Relaxation Processes*, **1**, 257 (1967).

Figure 1. Experimental setup for opto-acoustic spectroscopy.

Figure 2. Comparison of the carbon black opto-acoustic spectrum with that of a calibrated radiometer.

offers the possibility of observing absorption at the parts per 10^6 level or, for a gas at 1-atm pressure in the cell, the possibility of observing transitions with an oscillator strength of only 10^{-12} or so. This is the feature which first attracted us to the technique, but we have not yet realized the anticipated sensitivity.

Under what conditions does absorption lead to a signal at the microphone? In general, following electronic excitation, a molecule has three channels open to it: (i) it may luminesce, leaving little or no heat in the sample; (ii) it may undergo photochemistry, again leaving little or no heat in the sample; or (iii) it may do nothing, *i.e.*, cascade through the manifolds of electronic–vibrational–rotational levels to finally reach its ground state with the surrounding molecules concomitantly being heated. It is this part of the excitation energy, which is conventionally called the radiationless pathway, which Bell's technique monitors. Adapted to chemistry, it is the missing partner in luminescence and photochemical studies.

The most direct opto-acoustic effect is observed when the absorption is in a gas and that heated gas directly activates the microphone. Solids and liquid can be studied indirectly; their surfaces are heated by absorption and this then heats a transparent gas in contact with it and activates the microphone. We have not tried the technique on liquids yet, but Bell did report audible signals from colored solutions. For solids, the nature of the surface seems important. The more porous and the higher the surface area of the absorber, the stronger the opto-acoustic signal. Thus, we find the signal from soot to be a thousand times stronger than that from an aquadag layer. There seems to be no limit on the solids which can be studied in this way. We have successfully recorded the spectra of powdered $K_2Cr_2O_7$, flower petals, grass, dried blood smears, ultramarine, and carbon black.

There are, of course, a myriad of differences between opto-acoustic and regular absorption spectroscopy. One easily seen is that, whereas the photomultiplier response is proportional to the photon flux, the microphone response should be proportional to the optical power, *i.e.*, proportional to both the number of photons cm^{-2} sec^{-1} absorbed and to their frequency, since a photon at 3000 Å can result in twice as much heat as one at 6000 Å. In Figure 2, we compare the power spectrum of the lamp–monochromator combination as measured with a radiometer calibrated from 10,000 to 4000 Å, and the opto-acoustic signal of a sooty carbon black film measured with
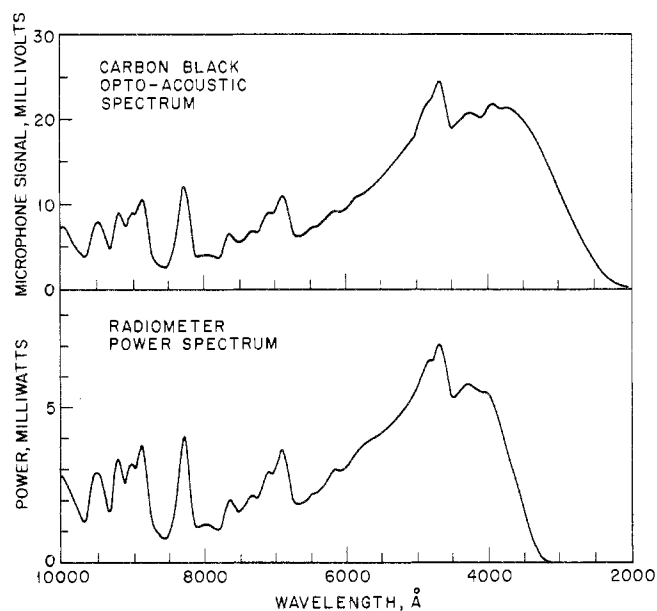
the same lamp and monochromator. One sees that, within the calibration range of the radiometer, the two spectra are virtually identical (except for a sharpness in the radiometer spectrum due to a shorter time constant).

This clearly demonstrates that the opto-acoustic spectrum is a power spectrum; in fact, the photon flux from our lamp in the 10,000- to 4000-Å range is a generally decreasing function, whereas the opto-acoustic signal is generally increasing in the same region due to the larger amount of heat released by the higher frequency photons. Note also that since the carbon black is near perfect in its absorption and subsequent heating as compared with the radiometer spectrum, it can be used as a reference channel in a double-beam opto-acoustic spectrometer.

We see from this that an absorption band profile in the opto-acoustic spectrum will appear distorted due to the fact that the high-frequency side of the band is absorbing more power than the low-frequency side. However, if normalized by dividing by the carbon black opto-acoustic spectrum, this factor is removed.

In the pages remaining to us, we present examples of the sorts of data the spectrometer generates, and also our own state-of-mind as regards interpretation.

We have found that the spectra of solids which are otherwise rather intractable can be easily obtained using opto-acoustic spectroscopy. Thus, in Figure 3 are shown the spectra of the flower petals of the black-eyed susan and of the red rose, and the opto-acoustic spectrum of the synthetic mineral Ultramarine Blue, obtained by replacing the mirror at the rear of the cell (Figure 1) by a glass plate upon which the sample is spread. The spectra in this figure have been corrected for the lamp output by manually dividing the sample spectra by that of carbon black.

In all of these spectra, the signal level was not particularly high, but we feel sure that a redesign of the cell which minimizes the volume of air between the
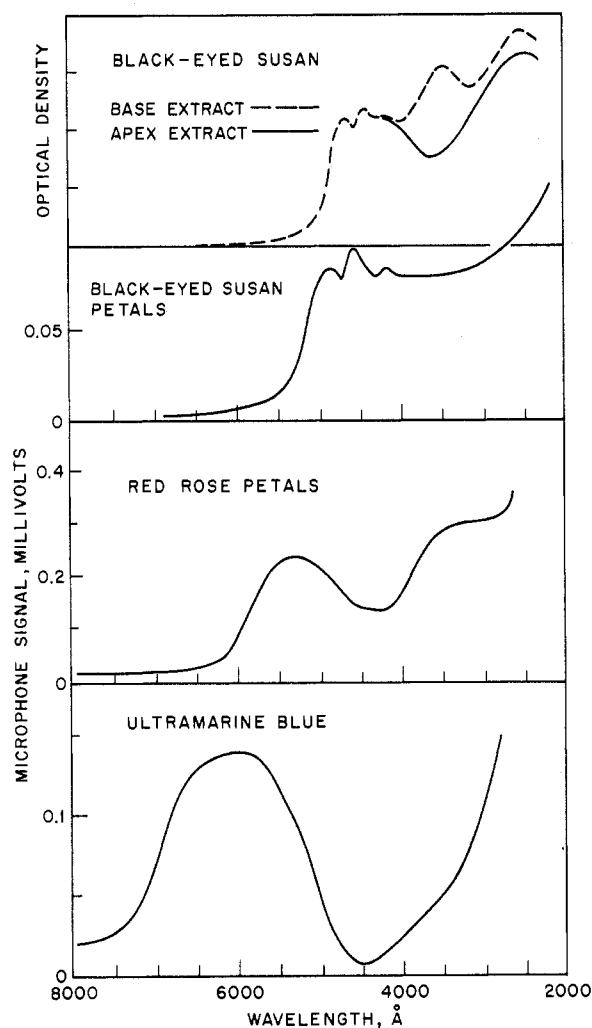
Figure 3. Opto-acoustic spectra of several solid samples. The spectra have been corrected for variations in the spectral output of the lamp by dividing by the opto-acoustic spectrum of carbon black.

microphone and the sample would increase the signal significantly. As in the ESCA spectroscopy of solids, it appears that the opto-acoustic signal transduced by the microphone originates in the outer layers of the solid. Thus, upon front-face illumination of a thin film of sooty carbon black on a quartz disk, a signal of 50 mV could easily be obtained, but upon illumination of the back surface through the quartz disk, the signal level was weaker by at least a factor of 10^{-5}.

Thompson, *et al.*,[9] have found that in the black-eyed susan the base of the flower petal is rich in ultraviolet-absorbing flavanol glucosides which serve as nectar guides to pollinating insects with ultraviolet vision. They extracted separately the bases and apices of the petals with methanol and obtained solution spectra in which both fractions showed the carotenoid absorption in the 4000–5000-Å region. But, whereas the apical extract shows a deep minimum at 3600 Å, the basal extract has a strong absorption maximum at 3500 A (Figure 3), due to the presence of the nectar guide in this part of the petal. In our opto-acoustic spectrum of the whole petals, we also

get the carotenoid spectrum (somewhat shifted), followed by what we take to be the average of the apical and basal extract solution spectra.

The coloring matter in red roses is typical of the plant pigments, being a substituted flavilium cation, called cyanine. Isolated from the flower, the solution spectrum of cyanine exhibits a strong maximum at 5300 Å and a second much weaker peak at 2750 Å, with a deep minimum at 3500 Å.[10] By contrast, the opto-acoustic spectrum of a rose petal also has a maximum at 5300 Å, followed by another strong one at 3400 Å; apparently the first maximum is due to cyanine absorption in the flower, but the second at 3400 Å must be due to some other ultraviolet-absorbing compound in the petal. Tentatively, one could argue that this band at 3400 Å in the rose petal is functioning as a nectar guide, much like the 3500-Å band in black-eyed susan.

Ultramarine blue (synthetic lapis lazuli) consists of a sodium aluminum silicate framework (colorless) forming cavities within which the blue ion S_2^- is entrapped. Its spectrum, as observed by reflected light in the 8000–4000-Å region,[11] is reported as having a broad maximum at 5900–6000 Å and a minimum at 4500 Å. The opto-acoustic spectrum (Figure 3) matches this description very nicely. At present, the opto-acoustic spectra of many other inorganic solids are being intensively investigated in our laboratory by Rosencwaig.[12]

Having mentioned above several diverse examples of the opto-acoustic effect in solids, we turn next to the spectra of gases where the unique features of opto-acoustic spectroscopy are best illustrated. As an example of the sensitivity of the opto-acoustic spectrometer, we have determined the absorption spectrum of the ethyl sulfide–iodine charge-transfer complex in the gas phase. This complex is a robust one $[K_c(298°) = 750]$ but has a very low vapor pressure.

Kroll[13] has studied this complex spectrophotometrically in the gas phase, but in order to achieve sufficient absorption he found it necessary to heat a 100-cm cell to between 90 and 150°. However, under these conditions an appreciable fraction of the complex is decomposed and the complex absorption then has to be separated from those of its components. In our experiment at 20°, we first observed the spectrum of iodine vapor (Figure 4) and then added ethyl sulfide vapor to the cell, whereupon the iodine absorption vanished completely and the charge transfer band appeared with a maximum at 3140 Å. This is just the wavelength at which Kroll found the charge-transfer band maximum in the high-temperature spectrum. The intensity of this band could be increased severalfold by preirradiation of the cell at 2400 Å for a few minutes.

Figure 5 compares the optical absorption spectrum of NO_2 (10 mm) with its opto-acoustic spectrum obtained using a double-beam spectrometer. Aside from the factor of relative spectral resolution, the

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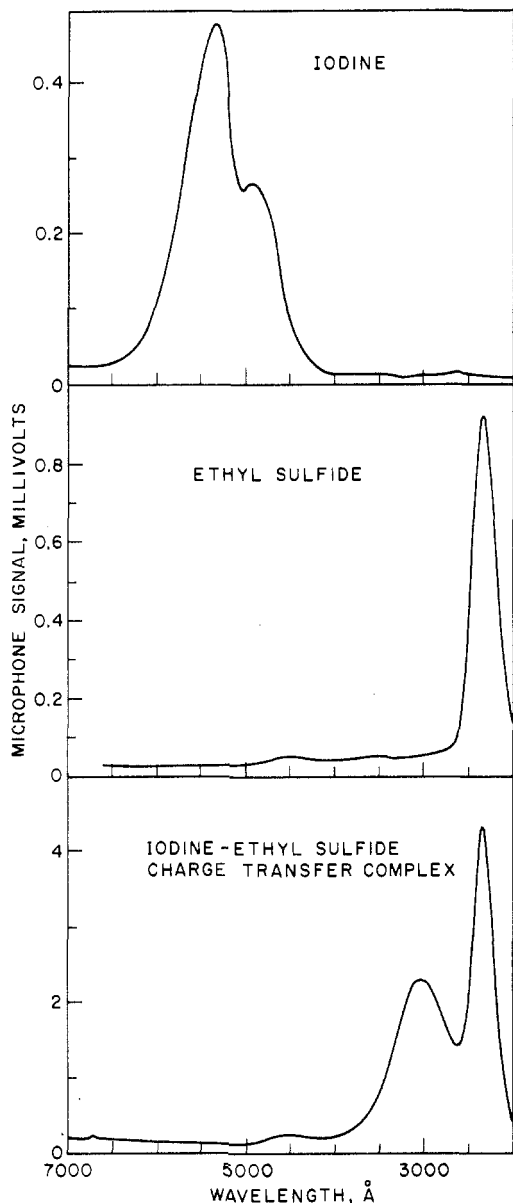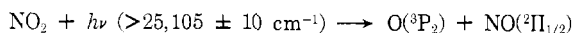(13) M. Kroll, *J. Amer. Chem. Soc.*, 90, 1097 (1968).

Figure 4. Opto-acoustic spectra of iodine and ethyl sulfide, and of the charge-transfer complex formed by mixing their vapors. In this figure, the iodine spectrum is distorted due to a trace of oxygen present in the cell as an impurity.

Figure 5. Comparison of the optical and opto-acoustic spectra of NO_2 at 10-mm pressure. The opto-acoustic spectrum was obtained using a double-beam spectrometer having carbon black in the reference channel.

general features of the two spectra look quite similar from 7000 to 4100 Å; however, at this point the opto-acoustic spectrum shows a sharp drop in signal strength which is not observed in the optical spectrum. This abrupt loss of part of the thermal signal is due to the fact that NO_2 dissociates at 3979 Å and below[14] according to

$$NO_2 + h\nu \ (>25,105 \pm 10 \ cm^{-1}) \longrightarrow O(^3P_2) + NO(^2\Pi_{1/2})$$

This dissociation is noted as the onset of diffuseness in the rotational fine structure of the high-resolution spectrum. However, in a conventional, low-resolution spectrum, as shown in Figure 5a, there is no indication of the onset of photodissociation of NO_2.

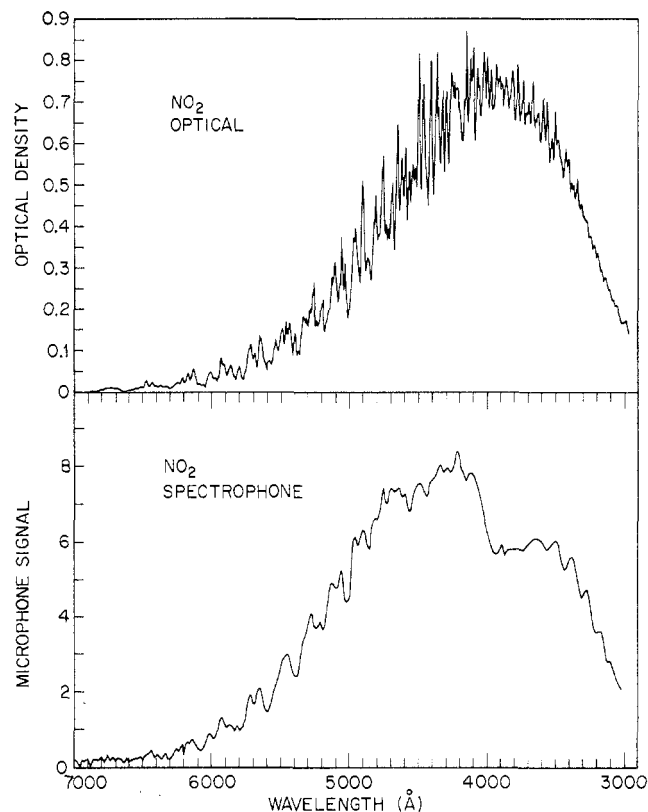Thus, we have a picture on which the optical energy absorbed at wavelengths larger than 4100 Å ap-

pears eventually as heat (there is no luminescence at our pressures), but once beyond the dissociation threshold, the optical energy instead is stored as chemical energy in the form of the ground-state fragments $O(^3P_2)$ and $NO(^2\Pi_{1/2})$, which themselves have only a slight excess thermal energy as they roll out of the upper state potential well. The discrepancy between the threshold of 3979 Å quoted above and the opto-acoustic dip beginning at 4100 Å is thought to be due to predissociation and to vibrational and rotational excitation in the ground state at room temperature. It is also interesting to note that approximately 75% of the opto-acoustic signal is still present above the dissociation limit. This could come either from the heat evolved from the rapid recombination of the NO and O fragments or, more likely, from the presence of other bound states in this spectral region.

Phase-sensitive detection of an opto-acoustic signal has been used for some time in infrared spectrophone experiments to measure the vibrational–translational relaxation rate.[8,15] In such experiments, the phase relationship between the pressure wave and the modulated light is given by $\tan \theta = \omega \tau / P$, where θ is the phase shift of the pressure signal at frequency ω in a gas at pressure P, and τ is the relaxation time for converting the energy of the excited state into translational energy.[15] Interestingly, we have noted in the opto-acoustic spectra of several gases

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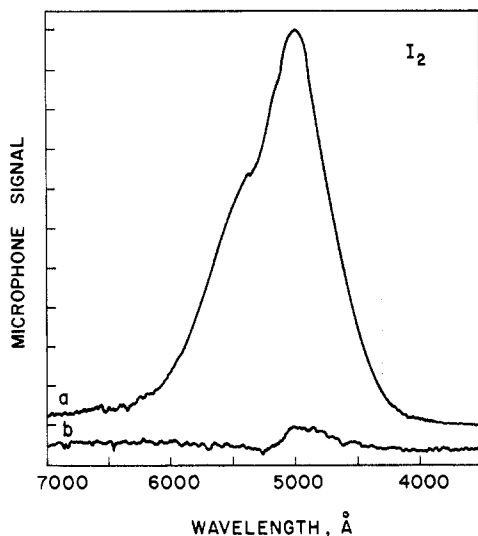
Figure 6. The opto-acoustic spectrum of iodine vapor in the in-phase (a) and out-of-phase (b) modes.

Figure 7. The opto-acoustic spectrum of sulfur dioxide, in phase multiplied ×25 to show the transition to $^3B_1$ (a), in phase (b), and out of phase (c). The spectra have not been corrected for the wavelength variation of the lamp intensity.

that the phase angle, θ, is dependent upon the wavelength of the exciting radiation.

This is illustrated most clearly in the opto-acoustic spectrum of iodine (Figure 6). In curve a, the phase angle, θ, of the lock-in amplifier was adjusted so that the signal at 5200 Å was maximal. The resulting opto-acoustic spectrum of I_2 resembles a conventional low-resolution absorption spectrum. Curve b was recorded after adjusting the phase angle to $\theta - 90°$. If the relaxation time τ were independent of the wavelength of the exciting radiation, the signal at $\theta - 90°$ would be nulled at all wavelengths. In fact, the out-of-phase spectrum ($\theta - 90°$) shows a difinite opto-acoustic signal beginning at 5200 Å.

Molecular iodine has three excited states which overlap one another in the spectral region of interest. The $^3\Pi_{1u}$ and the $^1\Pi_{1u}$ upper states are dissociative ($^2P_{3/2} + {}^2P_{3/2}$) with a separated-atom energy of 12,450 cm^{-1} above the molecular ground state. The $^3\Pi_{0u}{}^+$ excited state is bound, and correlates with the $^2P_{3/2}$ and $^2P_{1/2}$ atomic states at 20,037 cm^{-1}.[16,17] Thus, dissociation at wavelengths longer than 4990 Å leads to ground-state iodine atoms, but at shorter wavelengths the $^2P_{1/2}$ excited atomic state is produced. The out-of-phase signal in the opto-acoustic spectrum results from the heat released as the excited $^2P_{1/2}$ iodine atoms are relaxed to $^2P_{3/2}$. According to Husain and Donovan[18] this relaxation is accomplished with very high efficiency by collision with molecular iodine. Thus, the deexcitation of the $^2P_{1/2}$ atomic state must have a relaxation time significantly different from that of the $^3\Pi_{0u}{}^+$ molecular state, resulting in a phase shift of the spectrophone signal. However, at our low pressure of iodine (0.13 mm) and relatively slow chopping speed, it seems more likely that the out-of-phase signal is due to relaxation of I($^2P_{1/2}$) on the walls of the cell instead. In support of this, it is found that the amplitude of the
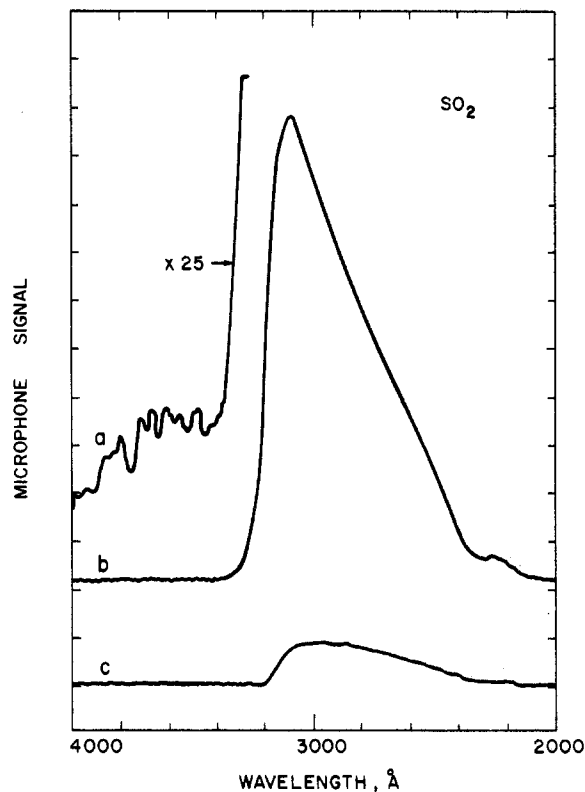
out-of-phase signal is dependent upon the prior treatment given the walls. The addition of a small amount of oxygen, which is known to very rapidly quench the excited $^2P_{1/2}$ iodine atoms,[18] results in a diminished opto-acoustic signal in the region of the spectrum where the excited iodine atoms are produced (Figure 4).

The opto-acoustic spectrum of SO_2 is our third example of the use of this technique to study radiationless transitions. In SO_2, there are three regions of absorption that are amenable to study with the present technique: the $^1A_1 \rightarrow {}^3B_1$ absorption in the region from 3900 to 3400 Å; the $^1A_1 \rightarrow {}^1B_1$ absorption in the region from 3400 to 2500 Å; and, finally, a cluster of intense bands starting at 2300 Å. The $^1A_1 \rightarrow {}^3B_1$ absorption, shown in Figure 7a, is quite weak, with an oscillator strength of 4×10^{-7}, whereas that for the $^1A_1 \rightarrow {}^1B_1$ transition is 5×10^{-3}, and that for the bands around 2000 Å is larger yet.[19] The SO_2 spectrophone signal shown in Figure 7b has not been corrected for the uneven background of the lamp output.

As shown in Figure 2, the lamp intensity is a monotonically decreasing function as the wavelength decreases from 4000 to 2000 Å. Thus, the lamp intensity distorts the shape of the $^1A_1 \rightarrow {}^1B_1$ band, resulting in a red shift of the opto-acoustical maximum. Though there is ample light at 2300-2000 Å to generate a strong opto-acoustical signal (as witnessed by the strong band observed in this region for

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Table I
Rate Constants for Relaxation of $^1SO_2$ ($^1B_1$) and $^3SO_2$ ($^3B_1$)
Following Illumination with Light at 3000 Å[22]

Reaction	k, l. (mol sec)$^{-1}$ or sec^{-1}
(1) $^1SO_2 + SO_2 \rightarrow 2SO_2$	$8.6 \pm 1.8 \times 10^{10}$
(2) $^1SO_2 + SO_2 \rightarrow {}^3SO_2 + SO_2$	$0.86 \pm 0.18 \times 10^{10}$
(3) $^1SO_2 \rightarrow SO_2 + h\nu_f$	$0.5 \pm 0.3 \times 10^4$
(4) $^1SO_2 \rightarrow (SO_2)$	$5.4 \pm 2.1 \times 10^4$
(5) $^1SO_2 \rightarrow {}^3SO_2$	$0.0 \pm 0.7 \times 10^4$
(6) $^3SO_2 \rightarrow SO_2 + h\nu_p$	$0.13 \pm 0.10 \times 10^3$
(7) $^3SO_2 \rightarrow (SO_2)$	$1.0 \pm 0.2 \times 10^3$
(8a) $^3SO_2 + SO_2 \rightarrow SO_3 + SO$ ⎫ (8b) $^3SO_2 + SO_2 \rightarrow (2SO_2)$ ⎬	$3.9 \pm 0.1 \times 10^8$

benzene), in SO_2 the intense absorption beginning at 2300 Å and peaking at *ca.* 2000 Å yields a relatively weak thermal signal (regardless of phase), which appears in the 2300–2200 Å region. The explanation here is that SO_2 molecules excited at 2206 Å and below are known to decay to ground-state SO and oxygen atoms with unit quantum efficiency,[20] thus completely depleting relaxation *via* the thermal channel, whereas above 2206 Å fluorescence is quenched at our high pressures, yielding heat,[21] but in a region of relatively low absorption.

Figure 7c shows the out-of-phase signal of the SO_2 opto-acoustic spectrum, recorded by nulling the signal at 3200 Å. As for the case of I_2, the phase angle of the thermal signal is dependent upon the exciting wavelength. Considering the pressures (1–760 mm) and chopping frequencies (10–1000 Hz) used in these experiments, it is concluded that the relaxation times must be longer than 10^{-6} sec in order to observe phase shifts of the magnitude shown in Figure 7.

Relaxation times for the conversion of electronic energy to translational energy have never previously been measured. However, Calvert and coworkers have made extensive studies of the quenching of luminescence from the excited states of SO_2.[22] Table I lists the quenching rate constants following irradiation with light at 3000 Å. These rate constants show that the quenching of $^1SO_2(^1B_1)$ is near the collision number and that 10% of $^1SO_2$ relaxes by an intersystem crossing mechanism to form $^3SO_2(^3B_1)$. At the pressures of the opto-acoustic experiments (1 to 760 mm), $^3SO_2$ relaxes by biomolecular processes. Otsuka and Calvert state that $^3SO_2$ is chemically quenched to form SO_3. At pressures above 5 mm, 70% of the $^3SO_2$ relaxes by the bimolecular reaction 8a of Table I.

The quenching processes listed in Table I are orders of magnitude faster than the processes that result in the phase-shifted signal of the opto-acoustic spectrum, since the opto-acoustic relaxation times must be longer than 10^{-6} sec. Furthermore, these spectrophone relaxation times are dependent upon the wavelength of the exciting radiation. Possible relaxation mechanisms which could explain the observed lifetime may involve the formation of dimers of excited SO_2. On the other hand, the relaxation times may reflect the vibrational relaxational processes in ground-state SO_2. We are currently studying the opto-acoustic spectrum of SO_2 as a function of pressure and chopping frequency in an attempt to further understand the relaxation mechanisms involved.

De Groot, *et al.*, have recently reported a study of the photochemistry of aldehydes using the opto-acoustic technique.[23] Using an experimental set-up quite similar to that shown in Figure 1, they studied the $n \rightarrow \pi^*$ absorption band of acetaldehyde. For an acetaldehyde pressure of 5 mm, the observed spectrophone spectrum looks quite similar to the optical spectrum, which has a maximum at 2900 Å. However, when the acetaldehyde pressure was increased to 60 mm, the opto-acoustic spectrum changed dramatically, showing a minimum near 2900 Å, rather than an absorption maximum. Approximately 65% of the absorbed light, under these conditions, was not accounted for by heat.

To explain the observed dependence of the spectrophone signal upon pressure and chopping frequency, De Groot, *et al.*, postulated the formation of dioxetanes as the relaxation mechanism of excited aldehydes at high pressures. We have since repeated these experiments and found at high pressures that the out-of-phase spectrum carries a large part of the heat missing in the in-phase spectrum, and that the entire effect is initiated by preirradiation which produces a very stable nonabsorbing species. If the sample is preirradiated at 100 mm so as to produce this species, and its pressure is then reduced to 10 mm, the typical "high-pressure" dip is still observed. Thus, the effect reported by De Groot, *et al.*, is confirmed, but is more complicated than first thought.

Conclusion

Although the opto-acoustic effect has been known for many years, the full potential of this technique has yet to be imagined, let alone realized as a spectroscopic tool. Our experiments show that the technique can give useful information about photochemistry, radiationless relaxation processes, and weakly allowed transitions when ultraviolet and visible light is used as the exciting radiation. In addition, this technique enables one to obtain the absorption spectrum of solids and amorphous substances directly. We confidently predict that the opto-acoustic effect will be used more broadly as a spectroscopic tool in the future than it was in the past 90 years since the discovery of the phenomenon.

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