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COMMENTS ON PHOTOACOUSTIC AND PHOTOTHERMAL SPECTROSCOPY OF GASES
COMPARED TO OPTICAL METHODS*

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Résumé - On analyse l'influence de quelques paramètres physiques (moment de transition, temps de relaxation, pression ...) qui conditionnent la sensibilité ultime des détecteurs photoacoustique et photothermique (PA/PT) que l'on compare aux méthodes de détection optique. On montre que c'est seulement à haute pression (faible résolution) et/ou pour des transitions faiblement autorisées que les méthodes PA et PT sont avantageuses en spectroscopie. Dans le domaine sous-Doppler on aura intérêt à utiliser une détection optique pour les transitions fortes et une détection bolométrique pour les transitions faibles.

Abstract - We discuss the influence of some critical parameters, especially the pressure, on the sensitivity of photoacoustic and photothermal methods for high resolution spectroscopy. We show that these methods lose their sensitivity in the sub-Doppler regime where they are advantageously replaced by optical detection (for which the shot noise limit can be reached with high frequency modulation techniques) or by detection of the internal excitation energy carried by the molecules onto a bolometer.

When one wishes to detect a weak absorption of light by a molecular gas, one can either measure the change in light intensity (transmission spectroscopy) or the change induced in the gas itself by molecular excitation (e.g. the pressure in photoacoustic spectroscopy).

The sensitivity of the first technique may appear to be poor because it is difficult to detect a small change on top of a large signal.

On the contrary, photoacoustic (PA) or photothermal (PT) detection as "dark background methods" have been broadly used in gas spectroscopy because they seem to exhibit a tremendous sensitivity especially when coupled with powerful laser sources. One knows, for instance, that atmospheric pollutants have been detected by this method at concentrations as low as a fraction of PPB [1]. Nevertheless one may wonder

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about the lack of success of these detection schemes in the field of very high resolution spectroscopy and more generally inquire about the parameters which affect the sensitivity of PA/PT experiments when compared to optical detection.

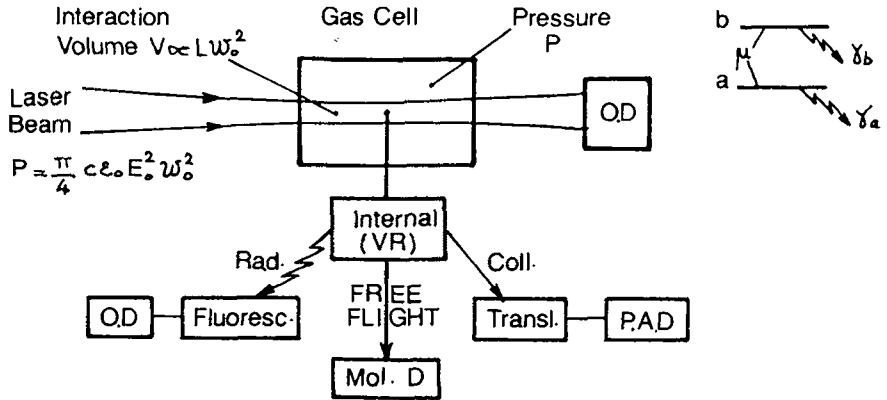


Fig. 1

In Fig. 1 we have represented the most simple situation where a laser beam of power $P = (\pi/4) c \epsilon_0 E_0^2 w_0^2$ (E_0 amplitude of the electric field, w_0 beam waist radius) is absorbed by the gas of an enclosed cell (length L) and the various ways of detecting the gas absorption :

- *By measuring the transmitted intensity with a suitable optical detector (OD),
- *By measuring the conversion of absorbed energy into translational degrees of freedom by photoacoustics in the collision regime (high pressure) or by molecular energy detection on the "walls" in the free-flight region (low pressure),
- *By measuring the fluorescence emission (at low pressure).

The molecular system is assumed to exhibit an optical transition at the laser frequency, between a lower state $|a\rangle$ and an upper state $|b\rangle$ whose relaxation rates are respectively γ_a and γ_b . We introduce an average transition moment μ from

the electric dipole operator $\vec{\mu}_{op}$:

$$\mu = \langle a J_a \parallel \mu_{op} \parallel b J_b \rangle / \sqrt{3g}$$

where g is a level degeneracy which we assume here to be same for both levels.

When studying this system from the point of view of a spectroscopist interested in the highest possible sensitivity one is led to ask the following key questions :

1) What maximum laser power P_{max} are we allowed to irradiate on the sample ?

The absorbed power (maximum signal power available) increases with the incident power and the limitation comes from the saturation of the absorption by the electromagnetic field. Indeed, the absorption starts to be strongly reduced and the line seriously power-broadened when the saturation parameter $S = \mu^2 E_0^2 T_1 T_2 / \hbar^2$ gets larger than 1. In this expression T_1 and T_2 are respectively the relaxation times of the energy and of the optical coherence and are given by :

$$T_1 = \frac{1}{2} \left(\frac{1}{\gamma_a} + \frac{1}{\gamma_b} \right) \quad T_2 = \frac{2}{\gamma_a + \gamma_b} = \frac{1}{\gamma_{ba}}$$

From the expressions of S and P we find the following value for the power corresponding to $S=1$:

$$P_{max} = \frac{\hbar}{16\alpha} \frac{e^2}{\mu^2} \frac{w_0^2}{T_1 T_2} = \pi^2 \hbar \omega \left(\frac{w_0}{\lambda} \right)^2 \frac{\tau_R}{T_1 T_2} \quad (1)$$

where α is the fine structure constant, e the electron charge and τ_R the radiative lifetime of the upper level (here τ_R is the reciprocal of the Einstein coefficient A_{ba} for the transition $b \rightarrow a$ only and is typically of the order of 0.01 to 0.1 second for strong vibration-rotation transitions).

In the collision broadening regime the relaxation rates are proportional to the pressure p (typically $\gamma_a/2\pi$ and $\gamma_b/2\pi$ are of the order of 10 MHz/Torr) and P_{max} is then proportional to p^{-2} . From (1) one can deduce that, at least for small values of the transition moment and in any case for pressures above one Torr, many watts of incident power may be used^(*) to excite the molecular system whereas usually optical detectors cannot stand more than a few mW.

(*) In this regime w_0 can be made as large as possible to optimize the total flux.

This point is obviously in favor of the PA/PT detection.

2) How much power ΔP is transferred from the light to the molecules and where does this power go ?

In the saturation limit ($S \sim 1$), the amount of power ΔP which is missing from the incident power P is of the order of :

$$\hbar \omega [n \cdot V] \frac{1}{T_1} \quad (2)$$

where n is the population of absorbing molecules per unit volume and where V is the interaction volume ($\sim L w_0^2$).

It is of interest to note that, because of the linear pressure dependence of n and $1/T_1$, ΔP is proportional to the square of the pressure. Also, in an ideal experiment the product $n \cdot L$ should be increased as much as possible to reach the limit $\Delta P \sim P_{\max}$.

ΔP is now available for the various channels of detection as shown in Fig. 1. Which channel is it better to use ? The answer has of course to do with the efficiency and the noise properties of each of them.

For high enough pressures collisions turn ΔP into local heating of the gas and the PA/PT detection channel is widely open.

3) What are the noise levels of the various detection channels ?

Using an optical detection, one deals with many kinds of noises [2] : Johnson noise, generation-recombination noise, $1/f$ noise, background-radiation noise and shot noise. To these we should also add the preamplifier noise and the laser power instabilities. When working properly (i.e. with suitable quantum detectors and filters cooled at liquid nitrogen or helium temperature, with suitable modulation or with high frequency heterodyne techniques) and above a given power level, the shot noise happens to be the ultimate limiting factor :

$$\Delta P_{\text{noise}} = (2 P B \hbar \nu / \eta)^{1/2} \quad (3)$$

where B is the bandwidth ($B = 1/4\tau$, τ integration time) and η the quantum efficiency of the detector.

Unfortunately in most experiments high frequency modulation of the absorption

is not possible and the fluctuations of the laser intensity are the major source of noise for direct optical detection (this "technical noise" has a large 1/f component and extends over a few MHz for dye lasers and a few tens of kilohertz for gas lasers).

In contrast to this case where the noise is proportional to the laser power and hence to the available signal power, dark-background methods offer a noise power which is, in first approximation, independent of the laser power^(*).

In a high performance photoacoustic cell (working at atmospheric pressure) limited by the Brownian motion of the gas molecules on the membrane of the microphone the noise is equivalent to 10^{-11} watt/ $\sqrt{\text{Hz}}$ [3] which is comparable to the photon shot noise power for P in the milliwatt range and, anyhow, much smaller than the technical noise power on the laser intensity.

Therefore, from the three points of view of available signal power, noise power and detection channel efficiency and, as far as high pressure experiments are concerned, PA/PT detection is more sensitive than classical optical detection, but what is going to change at lower pressure when resolution is needed?

4) What happens if we want resolution?

Let us recall that when reducing the pressure p in the cell one goes continuously from a collision regime (in which the lines are first pressure-broadened and then Doppler-broadened) to a free-flight regime suitable for ultra-high resolution sub-Doppler spectroscopy.

The main consequences of this pressure lowering are the following:

- The maximum laser power allowed by saturation decreases as p^2 (see § 1) dropping quickly in the milliwatt range in which optical detectors may be used. In the free-flight regime T_1 and T_2 are replaced by the average transit time w_0/u where u is the most probable velocity ($\sqrt{2kT/M}$) and formula (1) is replaced by the formula giving the π pulse power [4]:

$$P_{\pi} = \frac{\pi}{16} \frac{\hbar u^2}{\alpha(\mu/e)^2} = \pi^3 \hbar \omega \left(\frac{u}{\lambda}\right)^2 \tau_R \quad (4)$$

which can be as low as a few microwatts (e.g. SF₆ at 10 μm).

(*) Usually, however, practical limitations such as windows absorption may reduce the ultimate sensitivity of a PA cell.

- Since the absorption lines get narrower and narrower, high frequency modulation or optical heterodyne techniques can be used to get rid of the technical noise and to reach the photon shot noise limit [4]. Eventually this shot noise power will get smaller than the NEP of most PA/PT detectors. Combining formulas (1) or (4) with (3) we obtain interesting formulas for the signal-to-noise ratio :

$$\pi C \left(\frac{n}{2}\right)^{1/2} \left(\frac{w_0}{\lambda}\right) \frac{\tau_R^{1/2} B^{-1/2}}{(T_1 T_2)^{1/2}} \quad \text{for the collision regime}$$

$$\pi^{3/2} C \left(\frac{n}{2}\right)^{1/2} \left(\frac{u}{\lambda}\right) \tau_R^{1/2} B^{-1/2} \quad \text{for the free-flight regime}$$

where C is the signal contrast $\Delta P/P$.

- The absorbed power decreases as p^2 (see § 2) as long as the homogeneous width γ_{ba} is larger than the Doppler width ku . Beyond this limit only a small fraction $\delta v_z/u$ of the molecules available in the velocity space (z is along the optical axis) is used for absorption and since $\delta v_z \sim \gamma_{ba}/k$ in the collision regime this adds an extra power of p to the previous law. To compensate for this loss the only choice is to increase the interaction length L through multipass cells or Fabry-Perot resonators. But in any case the absorbed power cannot exceed P_{\max} given by (1) or (4) ($C \leq 1$).

- As the collision rate is reduced the amount of this absorbed energy which is converted into translational kinetic energy gets lower and lower and other detection channels take place such as fluorescence (e.g. saturated fluorescence of CO_2 has been widely used [5]).

As a consequence, when going to high resolution, as we turn the pressure down, there is always a crossover point for which optical detection is more sensitive than photoacoustic detection.

Moreover let us point out that sub-Doppler spectroscopy basically requires the smallest possible perturbations to molecular velocity (sensitive variable through the Doppler effect) which is completely antagonistic to the idea of transferring a noticeable part of the light energy into translational degrees of freedom. Thus PA detection of sub-Doppler resonances seems to be limited to pressures higher than

10-100 mTorr (even in this range optical detection of saturated absorption exhibits a much higher signal-to-noise ratio, at least for strong lines such as those of SF_6 , NH_3 or CH_3OH at 10 μm) for which the homogeneous width is in the MHz range, whereas optical detection has been proved to be suitable in the free-flight regime down to 10^{-6} Torr (with a linewidth in the sub-kilohertz range) [4].

At last, for very small dipole moments and correspondingly very long lifetimes both the usual PA/PT detection and optical methods break down at low pressures because of the very weak absorption over realistic optical paths and of the fact that all the internal energy is carried to the wall. One should then look for the absorbed power where it is, that is on the wall ! .

So, in order to extend the field of PA/PT high resolution spectroscopy of molecules, I would like to present an experiment which compares optical and thermal detections in the free-flight regime in which the absorbed energy is transferred away from where the molecules are excited. A supersonic molecular beam of SF_6 seeded in He interacts with a CO_2 laser beam perpendicular to its direction of propagation (Fig. 2). The absorbed power can be measured either by modulation of the molecular beam and detection on the optical detector (HgCdTe at 77K) or modulation of the optical beam and thermal detection with a bolometer (helium-cooled silicon chip) [6].

Thanks to a technique of interaction with four spatially-separated travelling waves (optical Ramsey fringes [4,7,8]) the linewidth can be reduced to 2.5 kHz (HWHM).

In the case of the SF_6 lines used in this experiment one still gets a higher signal-to-noise ratio with the optical detector (sensitivity in absorption of about 10^{-7} for $\tau = 1$ s) because these lines correspond to a rather large dipole moment (~ 0.21 D) for which the $\pi/2$ pulse power is only 32 μW .

Thanks to high frequency modulation of the molecular beam (1.5 kHz) one can reach the corresponding photon shot noise limit (within a factor 3) $\sim 10^{-12}$ W for one second averaging time. This noise power happens to be smaller than what can be achieved with usual bolometers used as detectors of excited molecules. Clearly this situation would be reversed with smaller dipole moments (and much larger laser

powers) for which the bolometer (optothermal) technique is presently the only way to achieve high resolution of weak vibration-rotation lines.

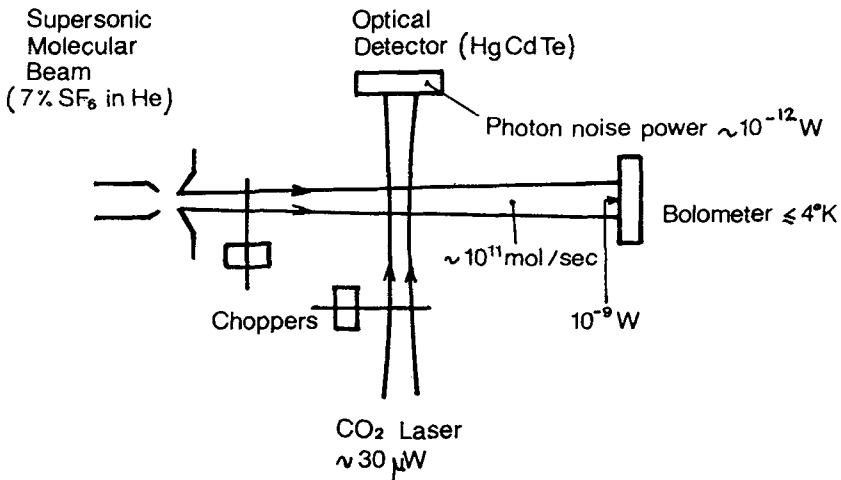


Fig. 2

In conclusion, the few considerations raised about the crucial pressure dependence of the PA/PT signal clearly indicate that the methods are highly competitive, when compared to optical detection, at high pressure (low resolution) and for weak transitions whereas they are not suitable for low pressure and high resolution experiments. The case of very weak transitions at ultra-high resolution is still an interesting challenge for experimental physicists and an active field of research for which the combination Ramsey fringes/bolometer appears as a promising method.

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