## Photopyroelectric detection of hydrogen/oxygen mixtures

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It has been found that the photopyroelectric (PPE) sensor made of thin-film polyvinylidene fluoride, sputter coated with palladium, can detect trace hydrogen gas in the presence of pure oxygen without significant drift and stabilization problems. Presently, hydrogen concentration as low as 0.1% in flowing 99.9% oxygen has been detected under standard temperature and pressure conditions. The detector has been used without a reference sensor (single mode) which simplifies the sensor system compared to previous work, at the expense of sensitivity limits. This paper describes the detection of hydrogen gas in hydrogen/oxygen mixtures, and deals with some instrumental aspects of the PPE sensor device such as background noise and signal drift. Some techniques for stabilization are also discussed.

## I. INTRODUCTION

Five years ago, in our laboratory, we undertook the task of developing and optimizing a fast, sensitive, and inexpensive photopyroelectric (PPE) sensor for trace hydrogen gas detection at room temperature.<sup>1-6</sup> During that time the base objective was to discover and prove the hydrogen sensing ability of the new device under ideal experimental conditions such as: (a) clean palladium surfaces, (b) room temperature, and (c) the minimization of any environmental impurities, in order to detect hydrogen in nitrogen ambient.<sup>1,2</sup> In 1990 in an extensive review paper we presented a critical comparison between the new PPE hydrogen sensor and other conventional devices.<sup>7</sup> Significant progress has been made both in the development and in the optimization of the new device,<sup>8</sup> as well as toward the understanding of the relevant physical mechanisms.<sup>9</sup> The PPE detector has been found to be able to operate through a broad range of temperatures (+53 to -60 °C)with a good potential for operation down to the liquidnitrogen temperature.<sup>8-10</sup> Broader interest in this photothermal device has been shown and a different version of our PPE sensor has already been built and used for hydrogen detection.11

Recently, hydrogen detection was studied under simulated ambient air conditions. This report describes the new results concerning these studies of the PPE hydrogen sensor for the detection of various concentrations of hydrogen gas in oxygen.

In this paper we point out the important capability of the device to detect reversibly low hydrogen concentrations in oxygen under room-temperature conditions. Seeing that the device sensitivity to hydrogen gas in pure nitrogen is much higher than in oxygen,<sup>2</sup> the present work is aimed at a "worst-case scenario" of hydrogen detection in pure oxygen. The commonly encountered situation of some level of H<sub>2</sub> gas in ~20% (140 Torr) O<sub>2</sub> in air is of intermediate sensitivity and a Pd-PPE sensor tested under pure oxygen flow-through conditions can only perform better in a mixture of oxygen and nitrogen ambient (e.g., air). Section II presents the experimental apparatus as well as some details of the test cell and optoelectronic system. In Sec. III we present experimental results for detection of hydrogen in oxygen. The observed sensitivity (1000 ppm  $H_2$  in  $O_2$ ) is 47 times higher than that required to monitor the critical explosive mixture of 4.85% hydrogen in oxygen. Information such as speed of response, reversibility, and durability are also discussed. Finally, Sec. IV presents some studies concerning the signal-to-noise ratio (SNR) optimization and response enhancement of the PPE device. This includes various types of signal drift, stabilization techniques, and some preliminary experiments concerning the influence of ambient temperature on the PPE signal.

Two major results were obtained.

(1) It was shown that, in terms of sensitivity and speed of response, the presence of oxygen does not introduce reversibility, reproducibility, and drift problems, when normalized signals are monitored. The sensor has been shown to be safe, in fact even mixtures including the explosive ratio have been safety checked (there are no ignition sources in PPE detection). The sensitivity of 1000 ppm in  $O_2$  under simulated dynamic flow-through ambient air conditions is very promising toward the establishment of a continuously monitoring H<sub>2</sub> sensor working at room temperature and in open atmospheric air, including the outdoors. The experiments performed under several hours and duty cycles prove that this device could be a valuable, real-time hydrogen detector. Signal stability improves with time after the system has been turned on.

(2) Several conclusions have been obtained concerning the SNR ratio optimization and response enhancement of the PPE hydrogen device: Three kinds of signal drift were identified: laser drift, background drift, and hydrogeninduced drift. The laser drift was eliminated simply by dividing the PPE signal by a part of the laser output. Nevertheless, before the starting of any experiment the system must be on for at least 20 min. The background drift can be minimized by careful metal deposition on the polyvinylidene fluoride (PVDF) at the fabrication stage. For stable measurements at low [H], it was shown that two neighboring Pd-PVDF detectors (active and reference) must be



FIG. 1. (a) Schematic diagram of the new photopyroelectric detector setup. (b) Schematic cross-sectional view of the new homemade test cell.

used differentially to offset the hydrogen-induced drift.

## **II. EXPERIMENTAL APPARATUS**

An experimental system has been constructed which has allowed us to test the response of the Pd-PVDF photopyroelectric sensor to flows of hydrogen, oxygen, nitrogen, and hydrogen/oxygen mixtures, with hydrogen concentrations ranging from 1000 ppm to pure hydrogen. The system has four subsystems: gas control; external temperature control, and test cell (internal) temperature control; fiber optic and laser system; and signal generation and analysis system [Fig. 1(a)]. This seemingly cumbersome apparatus may be much simplified in an actual sensing environment, once the controlled test cell, the reference sensor, the dc temperature controller, and the capacitance meter are removed. These were added in this work with a view to a much wider set of experiments than reported in this paper. Finally, miniaturization of the lock-in analyzer and the preamplifier<sup>8</sup> can further simplify the sensor circuit substantially.

## A. The gas control system

This system mixes the nitrogen and hydrogen gases in a homogeneous flow. The flow rate of each gas may be adjusted and stabilized before the mixture is directed into the test cell. The system includes tanks of pure oxygen, hydrogen-oxygen mixtures, nitrogen, and hydrogen gas; various pressure regulators in order to follow safety measures; and finally, three flow meters for measuring nitrogen, oxygen, and hydrogen gas flow rates, respectively. The gas handling system introduces a mixture of hydrogen and oxygen gases into the test cell and allows the mixture to leave through the exhaust lines. In fact, a metallic disk was installed in front of the gas inlet, in order to avoid some noise by dispersing the incoming gas to different directions in the test cell, thus obtaining a homogeneous stream [Fig. 1(b)].

### B. The temperature control system

The role of the temperature control system is to ensure that the temperature of the incoming gas flow will be the same as that of the sensor itself. A heat exchange coil was installed on the gas mixture line, upstream from the test cell in a water bath, in which the test cell and heat exchange coil were suspended in order to equalize their temperatures. Two thermocouples situated on the Inficon housing allowed the measurement of the bath and cell temperatures during our experiments. A heater was also added to the system to allow for testing at temperatures higher than ambient. Approximately one hour is needed for the heating element to increase the temperature from 20 to 60 °C by increasing the thermal flux controlled by a power supply. On the other hand, the new bath was designed and built so as to allow measurements down to liquid-nitrogen temperature (77 K). Adequate thermal insulation was added in order to thermally isolate the system.

### C. The test cell

The test cell is a pressure vessel which contains the active and reference PPE sensors, a special gas dispersion system, and simple heating elements. The new cell has the following features [Fig. 1(b)]: (i) Gas input/output nozzles. (ii) Six electrical BNC connectors: two connectors for the PPE signal, two for electrical resistive pyroelectric thermal-wave ac excitation, one connector for the inside thermocouple and one for the internal heating element. (iii) Two CANSTAR fiber optic adaptors (model ST) were adapted to the test cell in order to introduce laser light from outside without any gas or heat losses.

#### D. The signal generation and analysis setup

This is the basic optoelectronic signal part of the PPE hydrogen sensor described in Fig. 1(a). The optical system consists of a solid-state laser diode powered by an ac cur-



FIG. 2. Photopyroelectric response as a function of time in the presence of pure  $O_2$ .

rent supply (maximum output current of the laser power supply: 500 mA). The output laser beam, 100 mW *p-t-p* multimode at ~850 nm, was directed to a CANSTAR three-way fiber optic coupler (model MR-C-100/140). 45% of the optical beam was directed to each of the two detectors and 10% to the photodiode (PD) in order to monitor and correct the signal for laser output variations [see Fig. 1(b)]. The fiber optic core is 100  $\mu$ m in diameter, which matches the semiconductor laser fiber optic pigtail. This optical fiber can operate up to 125 °C<sup>12</sup> without optical transmission deterioration. Three different types of signals have been monitored in this report:

$$S_A = \frac{A}{R}, \quad \Delta S_R = \frac{A-B}{R}, \quad \Delta S_B = \frac{A-B}{B},$$
 (1)

where A and B were the signals obtained by the active and reference detector, respectively, and R was the ac laser power reference output obtained from the photodiode PD. More details on the signal generation and analysis have been given in previous reports.<sup>1,2</sup>

## **III. DETECTION OF HYDROGEN/OXYGEN MIXTURES**

# A. Hydrogen partial pressure measurements and sensor sensitivity

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Palladium-PVDF pyroelectric films were used (PD thickness: 1588 Å; PVDF film thickness: 52  $\mu$ m). For all experiments the gas flow rate was 500 ml/min.

Before the photopyroelectric response on hydrogenoxygen mixtures was studied, we checked whether pure oxygen underwent any reactions with the palladium-PVDF active elements, which might introduce signal shift. Thus, initially, pure oxygen flow was introduced through the test cell containing a clean Pd-PVDF film. Figure 2 shows the variation of the PPE signal as a function of time in the presence of  $O_2$ ,  $N_2$ , and again  $O_2$ , sequentially. No statistically significant change was observed. After this experiment the detector was exposed to various  $O_2/H_2$  mixtures.

Typical experimental results are shown in Figs. 3(a)-3(f) for various hydrogen concentrations. Figure 3 shows typical PPE responses as functions of time. Before each of the experiments the detector was cleaned for 30 min with pure oxygen. Then the prescribed flow rate of hydrogen (500 ml/min) was introduced to the test cell. In Figs. 3(a)-3(f), the variation of  $S_A$  as a function of time for hydrogen concentrations ranging from 100% to 0.1% (1000 ppm) is shown. The apparent discrepancy between the first and the subsequent signal saturation levels shown in Fig. 3(a) is due to the different gaseous ambients or trace amounts of H<sub>2</sub> in the air present in the cell before the introduction of H<sub>2</sub> gas. This effect illustrates the sensitivity of the Pd-PPE sensor to the presence of inert gaseous constituents in the ambient. Figure 3(b) presents only two cycles (first and second) of a long experiment of  $\sim 7$  h duration, which have proved the complete reproducibility and reversibility of the photopyroelectric device in an oxygen/hydrogen mixture at room temperature. Similar results were obtained through cycling with the other  $[H_2]/[O_2]$  ratios in Fig. 3 and will be discussed later on. Fig. 3(f) is extremely difficult to obtain in the  $S_A$  signal mode and sometimes irreproducible. For those low detection levels high stabilization of the device is needed. This will be discussed in the next section. In Fig. 3 it is seen that after the interruption of  $H_2$  and the introduction of pure oxygen, and before the signal reaches the saturation level, there appears an intermediate signal "induction" period. Figures 3(a)-3(d) clearly show that at high  $[H_2]/[O_2]$  ratios the delayed induction feature is reproducible and the duration of the effect increases with decreasing  $[H_2]$ , which suggests that it is related to the hydrogen-Pd surface interaction. At low [H<sub>2</sub>] concentrations in hydrogen/oxygen mixtures, Figs. 3(e) and 3(f), the presence of this induction period is not well pronounced. It is probable that this signal saturation delay observed in the case of high concentrations of hydrogen in oxygen is due to the production of water on the Pd surface. If this is so, there is no evidence of cumulative surface water effect on the reversibility of our signals, as discussed above. Another possibility for the observed induction period might be the phase transition of Pd from  $\alpha$  to  $\beta$  form in the presence of hydrogen in the bulk. This effect, however, is known to occur at lower hydrogen concentrations ( $\leq 2000 \text{ ppm}$ )<sup>13</sup> and has not been observed with the photopyroelectric sensor in  $H_2/N_2$  mixtures in the concentration range of Figs. 3(a)-3(c).<sup>2</sup> In a recent publication Hughes and Schubert<sup>14</sup> used thin allow films of Pd and Ni (8% < Ni < 20% in at. %), capable of suppressing the  $\alpha$  to  $\beta$  phase transition found in pure Pd under high  $H_2$  concentration conditions (>0.1%). Figure 4 shows the variation of the saturated photopyroelectric signal,  $\Delta S_S$  (see schematic definition in Fig. 5) as a function of hydrogen concentration. Note that  $\Delta S_{S}$  increases monotonically when the hydrogen concentration increases, while the lowest (0.1%) hydrogen concentration signal is not believed to be an absolute minimum. Differential signal

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FIG. 3. Photopyroelectric signal ratio (A/R) as a function of time for six different concentrations of hydrogen in oxygen.

detection is expected to improve this level of sensitivity. Lundström and Soderberg have succeeded in detecting much lower concentrations of hydrogen in oxygen (a few ppm) by using a metal-oxide-semiconductor (MOS) device.<sup>15</sup> Nevertheless, there are some fundamental differences between our experimental methodology and theirs. Lundström and Soderberg, as well as several other researchers in the field of hydrogen detection, performed

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their experiments under very specific laboratory conditions such as UHV, high temperature, clean surfaces, and static gas conditions. As the authors admitted these conditions "are often far from those encountered when a Pd-MOS device is used as a practical sensor." On the other hand, we present results, which have been obtained from a detector relatively open to the environment, at room temperature, and without any active surface conditioning.

The surface Langmuirian monolayer analysis presented by Lundström and Soderberg cannot be applied in our case for at least three reasons: (a) We used no high ambient control conditions (UHV) but just standard temperature and pressure (STP); (b) The working roomtemperature conditions of this work may necessitate completely different analysis of the two types of hydrogenoxygen reaction mechanisms presented by the above authors, since we do not have as a reaction product H<sub>2</sub>O gas, but liquid water; and (c) The results of Fig. 4 are out of the range of the monolayer model ( $\leq 1500$  ppm). The critical limit of 1500 ppm has been obtained upon extrapolation of the Langmuir isotherms presented by Lundström and Soderberg:<sup>15</sup> It has been shown by the above authors that in the case of hydrogen detection in air, and when the oxygen percentage in the mixture is over 1%, the response signal reaches saturation; therefore, the monolayer model cannot be applied over this limit. In view of the similarity between the isotherm shown in Fig. 4 and recent results reported for the Pd-Ni thin-film chemiresistor fabricated by Hughes and Schubert,<sup>14</sup> it is likely that the bulk resistance change of Pd in the presence of hydrogen absorbed into the bulk Pd of the chemiresistor may have common origin with the observed PPE signal in this work. Bulk hydrogen absorption in the Pd coating of our PVDF sensor, in addition to well-known electrical changes,<sup>9</sup> may also cause a large volume change, roughly proportional to the [H]/[Pd] ratio. The change in Pd coating dimensions could cause unbalanced stresses at the Pd-PVDF interface, resulting in a change in the pyroelectric coefficient.

#### B. Speed of response and recovery time

The response time and the recovery time are defined, respectively, as the time which is required for the rising signal to reach saturation (i.e., steady state), and the time which is required for the saturation state to return to the original baseline (see Fig. 5). Figure 6 shows the variation of the response and recovery times  $R_S$  and  $R_C$ , respectively, as functions of the hydrogen concentration. We note that  $R_S$  varies strongly as a function of [H], as was expected. On the other hand,  $R_C$  does not seem to be related to the hydrogen concentration. In fact, the recovery time is artificial and depends on the experimental conditions. For example, it was shown by Christofides and Mandelis<sup>1</sup> that if one evacuates the cell from hydrogen gas by using an exhaust pump, the outflow rate of the gas affects (reduces) the value of  $R_C$  substantially.



FIG. 4. Photopyroelectric saturated signal  $(\Delta S_S)$  as a function of hydrogen concentration. The solid lines present the error at low and at high concentrations.

#### C. Sensor reversibility and reproducibility

Figure 7(a) shows the excellent reproducibility of the PPE saturated signal  $(\Delta S_A)_S \equiv \Delta S_S / R$  after many cycles of exposure to hydrogen ([H]=50%) at room temperature (see Fig. 5 for the definition of duty "cycle"). The points of Fig. 7(a) were found by subtraction of the minima from the maxima of Fig. 7(b) (see Fig. 5 where minima and maxima are defined). In terms of reversibility, the signal quality shown in Fig. 7 lasted several exposures, over the span of almost 7 h under various hydrogen concentrations in pure oxygen. Thus, reversibility and reproducibility of the photopyroelectric signal in the presence of oxygen has been successfully demonstrated in this work and opens the way for photopyroelectric measurements under real, rather than simulated, ambient conditions.

In Fig. 7(b) one can see the values of the minima and maxima of ten sequential cycles. We note that both max-



FIG. 5. Schematic definition of  $R_s$  (response time),  $R_c$  (recovery time),  $\Delta S_S$  (saturation level), minimum, maximum, and duty cycle.



FIG. 6. Variation of response time  $R_S$  and recovery time  $R_C$  as a function of hydrogen concentration.



FIG. 7. (a) Photopyroelectric saturated signal  $(\Delta S_A)_S$  as a function of cycle number. (b) Temporal evolution of several cycles before subtraction of the base line.



FIG. 8. Variation of response time  $R_S$  and recovery time  $R_C$  as a function of cycle number.

ima and minima decrease monotonically with time and duty cycle due to the background drift of the PPE signal. On the other hand, the differences between these maxima and minima,  $(\Delta S_A)_S$ , remain essentially constant for each cycle, as was shown in Fig. 7(a).

Figure 8 shows the variations of  $R_S$  and  $R_C$  as functions of cycle number and time. On the average, both response and recovery times are independent of duty cycle number, as expected.

## IV. SIGNAL DRIFTS, OPTIMIZATION, AND STABILIZATION OF THE PPE HYDROGEN DEVICE

## A. Nature of PPE signal drift

As is well known, some of the main problems that appear in MOS hydrogen devices in relation to the monitoring of hydrogen concentrations are the serious signal drifts which these devices present. According to Choi et al.,16 "despite the high sensitivity of these devices, they are still not very useful for monitoring hydrogen leaks." These nondesirable drifts have been the object of several researches during the last ten years.<sup>17,18</sup> According to those results, the blister formation on the Pd-gate metal is the main cause of the deterioration of sensitivity with time of the semiconductor-based devices, because they introduce a certain lattice expansion of the Pd-gate film. Choi et al.<sup>16</sup> and Armgarth and Nylander<sup>17</sup> do suggest, however, ways to circumvent the problems of blister formation. This, in all likelihood, has been achieved in commercial Pd-MOS devices currently available from Sweden.<sup>19</sup> Another very serious signal drift of the MOS devices is the one related to charging of the oxide in the presence of hydrogen. Ultimately, it is this drift (named HID: hydrogen-induced drift) which seriously limits the suitability of those sensors as commercial devices for continuous gas monitoring applications.<sup>16</sup>

Figure 9 presents the variation of the PPE signal as a function of time. At time t=0, the system [including the detection electronics, Fig. 1(a)] was turned on. Note that during the first hour the signal drift is at least twice as large as that during the third hour of operation. In fact, during

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FIG. 9. Normalized photopyroelectric signal variation as a function of time. At time t=0 the device was turned on.

the entire research undertaken so far toward the development of the Pd-PVDF sensor, some signal drift was one of the problems faced early on by our device. Fortunately, this problem will be shown here to be under effective control. We can distinguish three main causes of signal drift: (i) drift related to the variation of the laser output, (ii) drift associated only with the photopyroelectric background signal, and (iii) drift related to the introduction of hydrogen. These will be identified as laser drift, background drift, and hydrogen-induced drift, respectively.

(a) Laser drift. One of the main problems which the PPE device may present has to do with the stability of the laser output. This must be constant, in order to have a (ideally) nonvariable PPE signal. Experience has shown that the time history of the laser output plays a significant role in the stability of the device: Before any experiments are carried out, it is necessary to leave the semiconductor laser on long enough for it to thermalize and reach stabilization. Furthermore, the stabilization time increases with the age of the laser. This drift-inducing mechanism can be eliminated simply by dividing the PPE signal by a part of the laser output (signal  $S_A$ ). This technique has been used effectively from the beginning of the development of the Pd-PPE sensor.<sup>1,2</sup>

(b) Background drift. This drift has two main possible sources: (1) PVDF fabrication conditions regarding the Pd deposition, and (2) adsorbed/absorbed/ desorbed gaseous impurities. It is well known that the conditions of the metal deposition on the PVDF play a very important role toward the quality of the PPE signal.<sup>20,21</sup> Recently, we found that the drift problem can be eliminated by cutting two film disks from the same PVDF film sheet and from adjacent locations. During the earlier stages of this work we used one active Pd-PVDF and one reference Al-Ni-PVDF, from a different PVDF sheet. However, this is not optimum in the light of our recent results, since metal deposition in these films was done under different conditions. Consequently, in this work we used two neighboring Pd-PVDF films, one of which had access to its surface by the gas blocked, thus acting as a reference. Two such elements are likely to be similar, since they are subjected exactly to the same poling and deposition conditions (electric field, temperature, and time). By comparing the behavior of these films it has been found that they have the same signal drift in time. The reasons for this similitude may be related to the inhomogeneous poling profiles existing in commercial PVDF films,<sup>22</sup> which potentially vary from one PVDF sheet to another. The second cause of the drift may be due to the contamination of the Pd surface under ambient conditions.<sup>13</sup>

(c) Hydrogen-induced drift. From the foregoing it may be concluded that the use of two Pd-PVDF detectors cut from adjacent strips on a PVDF sheet is very important for precise and continuous monitoring of hydrogen concentrations. One of the detectors was isolated from hydrogen by placing on top of the Pd surface a thin piece of glass (e.g., microscope slip). Figure 10 shows the variation of the normalized PPE signal as a function of time under different instrumental and reference conditions. Before these experiments, the detector had been switched on for  $\sim 1$  h in order to reach stabilization. Then, pure oxygen was introduced to the test cell. We noted that the signal changed drastically in the beginning. This might be due to the cleaning of the Pd surface. From these observations it was concluded that our sensor performs best under continuous monitoring conditions, with the system being continuously on.

In Fig. 10 signals have been normalized as shown, with the average values of ten sampled points shown at each recorded time interval for various normalization ratios. From Fig. 10(a) it is seen that the ratio [(A-B)/R] is more stable at 32 Hz than at 17 Hz, which is close to the thermally thin/thick limit.<sup>23</sup> It is possible that the higher noise level at 17 Hz is due to lower transfer function SNR of the detection electronics (PVDF capacitor-preamplifierlock-in analyzer), even though the absolute magnitude of the photothermal signal is substantially higher than that at 32 Hz. In fact, it has been found that the signal change in Fig. 10(a) is 13% and 9% at 17 and 32 Hz, respectively. On the other hand, between the two ratios [(A-B)/B]shown in Fig. 10(b), the one which was obtained from the two neighboring Pd-PVDF detectors of the same film is more stable as expected with a 3% change (vs 6.5% change of the Pd-Al pair) over the observation time span of Fig. 10(b).

# B. Recognition of $(S_A)_S$ in the presence of background drift

Figure 11 presents a schematic of the evolution of the photopyroelectric signal as a function of time. One can distinguish two cases: (a) the ideal one, without any drift, and (b) the case where drift is present. In the "ideal" case one can distinguish the PPE hydrogen response very easily. For the detection of high concentrations of hydrogen, even if there is a certain background drift, the response dominates the change due to the drift and the "ideal case" can

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FIG. 10. (a) Normalized photopyroelectric signal  $\Delta S_R$  variation as a function of time for two frequencies and two normalization procedures using different PVDF films (see text). (b) Normalized photopyroelectric signal  $\Delta S_B$  variation for two different PVDF reference sensors: (i) from Pd-PVDF film adjacent to the active element; and (ii) from Al-Ni-PVDF film. In (a) and (b) the signals have been artificially separated out for clarity.

still be applied for the definition of  $\Delta S_S$  from a single sensor, without any signal normalization except for laser intensity fluctuations  $(S_A)$ . On the other hand, in the case where there is a strong presence of drift or one wants to detect low hydrogen concentrations, with a single sensor, where the response is so small that it is dominated by the drift, one can note that the introduction of hydrogen to the cell changes the slope of the photopyroelectric signal as a function of time. The slope changes with the introduction of hydrogen and returns to the initial value after the interruption of the hydrogen gas. In Fig. 12 one can see the procedure for measuring the saturated photopyroelectric signal  $\Delta S_S$  in the case where the hydrogen response is dominated by the background signal drift. Some of the [H] data points presented in Fig. 4 for low hydrogen concentrations (0.1%) were obtained by using the above tech-



FIG. 11. PPE schematic of hydrogen response as a function of time: (a) case of constant background and (b) with drifting background.

nique of slope measurement of the PPE signal change due to the superposition of system drift plus the presence of hydrogen. Figure 12 shows the application of the schematic in Fig. 11 toward the measurement of  $(\Delta S_A)_S$  in 0.1% hydrogen in oxygen.

#### C. Temperature and background drift

Figure 13 shows the variation of the PPE signal  $S_A = A/R$  as a function of time. The signal had been stabilized at T = 20 °C before ramping up the temperature and no significant instrumental background was registered. Subsequently, the signal became very noisy at the onset of increase of the cell temperature. The PPE sensor was thus seen to need at least one hour of stabilization before it is able to detect concentrations lower than 0.5% of H<sub>2</sub> in O<sub>2</sub> at elevated temperatures. Some preliminary results with a LiTaO<sub>3</sub> PPE sensor have shown similar relaxation times



FIG. 12. Photopyroelectric signal ratio  $S_A$  as a function of time in the case of the presence of a strong background drift. 0.1% hydrogen in oxygen.

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FIG. 13. Variation of the photopyroelectric signal as a function of increasing cell temperature.

(at high temperatures) as the PVDF thin films. LiTaO<sub>3</sub> crystal pyroelectrics have a clear advantage when high temperatures (>100 °C) must be employed, which is not the case here, since we were able to obtain high quality, reversible signals at room temperature. In terms of safety against hydrogen-induced explosions nucleated by electrical sparks, the present Pd-PVDF sensor ranks well with the all-optical fiber-optic sensor developed by Butler:<sup>24</sup> the exciting optical pulse is completely inert electrically, while no electrical discharge is possible across the leads of the PVDF film output, since the laser diode power supply can be located quite remotely from the sensing environment.

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