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Optimization of the Optothermal Detector for Absorption Spectroscopy in the Low Pressure Range

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Abstract. To use the sensitivity and the measurement accuracy of the optothermal detector (OT) better for linear absorption detection, a theory of the signal behaviour, worth for the most important range of application, is developed and compared with experimental data. By means of the example of CO_2-laser light absorption by ammonia, containing two different nitrogen isotopes, the possibility of correcting measured values to get more exact information of the absorption behaviour is shown. The limits of error, as well as the reproducibility of the measurements could be kept in a range of about 1%.

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The optothermal (OT) detector provides the possibility of direct detection of absorption of gases in such pressure ranges, where the free path length of the particles is above as well as below characteristic lengths of the dector. This has been shown in [1, 2]. Still, if quantitative information of the absorption behaviour of the gas shall be obtained, the dependence of the OT signal on the parameters of the gas to be measured and on the construction of the OT detector needs to be known. The purpose of this article is the calculation of this dependence in the pressure range, in which the thermal conducting is dominating, and its application to the measured data of ammonia. Furthermore, the possibility of measuring absorption reproducibly shall be shown.

1. Theory of Heat Conduction in a OT Detector

According to Rosengren [3] the OT detector works on the base of measuring the variation of gas temperature after absorption of light energy from a laser beam with modulated power. According to [1], there is no need for relaxation of the exciting energy to get thermal energy as kinetic energy of molecules, but this energy also can be detected by relaxation of the molecules on the surface of the pyrodetectors, when they are arranged around the laser beam. The foundation for the efficiency of this method is a relaxation of the excited particles without radiation, i.e., the relaxation of the excited states happens by collisions of the particles among one another or with the detector surface. It is advantageous to use pyrodetectors with a large surface, e.g. thin foils. Below a certain gas pressure depending on the dimensions of the OT detector, the temperature variation of the foils is determined by conducting heat or by collisionless transport of the exciting energy onto foils. When the foils are arranged at the radius R_2 (Fig. 1) and when the measures of the housing including the gas are neglected (dimensions $\rightarrow \infty$), the temperature variation of the gas can be expressed by the thermal diffusion equation

$$\frac{\partial T_1}{\partial t} = \frac{\lambda R T_1}{p C_p} \Delta T_1 + \frac{\alpha P R T_1}{\pi R_1^2 p C_p} \quad \text{(inside the beam)}, \qquad (1)$$

$$\frac{\partial T_2}{\partial t} = \frac{\lambda R T_2}{p C_p} \Delta T_2 \quad \text{(outside the beam)} \qquad (2)$$

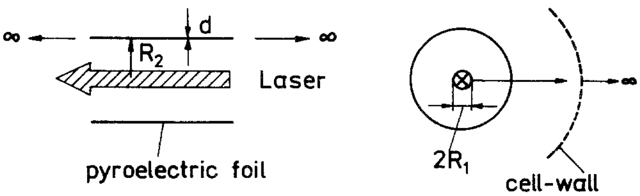

Fig. 1. Design of the OT detector

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with the boundary conditions

$$T_1|_{R_1} = T_2|_{R_2}\,; \quad \left.\frac{\partial T_1}{\partial r}\right|_{R_1} = \left.\frac{\partial T_2}{\partial r}\right|_{R_1}.$$

In (1) and (2) there is λ the heat conductivity of the gas, R the universal gas constant, $T_{1,2}$ the gas temperature, p the gas pressure, C_p the molare specific heat under constant pressure, α the absorption coefficient, and P the laser power. When the excited states do not relax, i.e., when the pressure is so low that not enough collisions of the gas particles for relaxation take place, in these equations the temperature is a fictive parameter. $T_{1,2}$ is here the temperature that would be reached, if the energy absorbed by the particles relaxed. Equations (1) and (2) are not valid, when the medium free path length comes into the order of magnitude of R_2 or is greater. The pyroelectric foil receives the heat current

$$I = j \cdot 2\pi R_2 l\,,$$

where

$$j = -\lambda \left.\frac{\partial T_2}{\partial r}\right|_{R_2}.$$

If the foil is a sink for the heat current, the temperature of the foil will be determined by this current and by the capacitive heat impedance of the foil. In [4] there has been shown that the foil can be treated as a heat sink under the following conditions: its thickness d has to be small compared to the thermal wavelength in the pyroelectric material at the modulation frequency $\omega = 2\pi f$ of the laser power,

$$d < (\lambda_F / \omega c_F \varrho_F)^{1/2}$$

(λ_F being the heat conductivity, c_F the specific heat capacity and ϱ_F the mass density of the foil material), and its heat capacity $K_F = 2\pi R_2 l d c_F \varrho_F$ has to be large compared to the heat capacity of the gas, which loses its energy on the foil in the time of one modulation period $\tau = 2\pi/\omega$. The last condition defines a lower limit for d

$$d \gg (\lambda p C_p / \omega R T)^{1/2} \cdot (c_F \varrho_F)^{-1}\,.$$

Both the inequalities are fulfilled for the thickness of the used foil, $d = 10^{-5}$m, and the experimental data $\lambda_F = 3 \times 10^{-1}$ W/mK, $\omega = 200$Hz, $c_F \varrho_F = 2 \times 10^6$ Ws/m^{3}K, $C_p = 29$Ws/MolK, $T = 300$K, and $p \leqq 10^5$Pa. Therefore, the temperature of the foil can be written as

$$T_F = \mathrm{i}\frac{\lambda}{c_F \varrho_F d \omega}\left.\left(\frac{\partial T_2}{\partial r}\right)\right|_{R_2} + T_0\,. \tag{3}$$

When the modulation of the laser power is supposed as $P = P_0 \exp(\mathrm{i}\omega t)$, the solution of (1) and (2) has the form

$$T_{1,2} = A_{1,2} \exp(\mathrm{i}\omega t) + T_0\,.$$

In the case $|A_{1,2}| \ll T_0$, T_F will be

$$T_F = -\delta\gamma\left[\frac{\mathrm{Y}'_{02}\mathrm{J}'_{01}}{\mathrm{Y}'_{01}\mathrm{J}_{01} - \mathrm{Y}_{01}\mathrm{J}'_{01}} - \frac{(\mathrm{Y}_{02} + \delta \mathrm{Y}'_{02})(\mathrm{J}'_{02}\mathrm{J}'_{01})}{([\mathrm{Y}'_{01}]\mathrm{J}_{01} - \mathrm{Y}_{01}\mathrm{J}'_{01})(\mathrm{J}_{02} + \delta \mathrm{J}'_{02})}\right] + T_0\,. \tag{4}$$

The symbols I_0, Y_0, I'_0, Y'_0 mean the Bessel and Weber function of order zero and their first derivation at the radii R_1 and R_2. The argument of these functions is expressed by

$$R_{1,2} \cdot (-\omega p C_p / \lambda R T_0)^{1/2}\,.$$

Furthermore

$$\delta = -\mathrm{i}(\lambda / c_F \varrho_F d \omega)(-\mathrm{i}\omega p C_p / \lambda R T_0)^{1/2}$$

and

$$\gamma = \mathrm{i}\alpha P_0 R T_0 / \pi R_1^2 \omega p C_p\,.$$

The temperature variation $\Delta T_F = T_F - T_0$ is an expression of complex numbers, describing amplitude and phase of the signal. The analysis shows that ΔT_F reaches a finite value, when p goes to zero, and goes to infinite, when ω goes to zero. When the argument is smaller than one, the temperature variation of the foil does not depend on the gas pressure and on other gas parameters.

The argument being smaller than one means that there are no thermal waves in the gas, i.e., the phase of the temperature in the gas is the same as the phase of the modulation. The magnitude ΔT_F in this range is determined above all by the heat capacity of the foils and by the modulation frequency, but hardly by the gas parameters and the laser-beam radius. The condition stated above for the argument leads to a condition for the radius R_2, where the foil is arranged, i.e.,

$$R_2 < (\lambda R T_0 / 2\omega p C_p)^{1/2}\,. \tag{5}$$

For an OT detector desired to measure independently on kind of gas up to 1.3×10^2Pa, there must be, for instance, $R_2 < 6 \times 10^{-3}$m, with $\lambda = 2.6 \times 10^{-2}$W/mK (air), $R = 8.3$Ws/KMol, $T_0 = 300K$, $\omega = 200$Hz, and $C_p = 29$Ws/KMol. At the end of this discussion, it shall be stressed that (4) describes the behaviour of the OT detector with good accuracy only, when condition (5) is fulfilled. At a greater pressure for the analysis of the OT problem the additional temperature variation of the gas by its adiabatic compression and expansion must be considered.

2. Comparison with Experimental Data

To gain a suitable insight into the pressure-signal characteristic and to compare it to the experimental behaviour of the OT detector, (4) has been calculated numerically for the construction used for the experiment with $R_2 = 1.1 \times 10^{-2}$m, $d = 2 \times 10^{-5}$m, $\omega = 200$Hz, and $P = \text{const}$. The result of this calculation is shown in the Fig. 2 by the solid curves for the amplitude as well as for the signal phase.

The represented pressure range extends up to such values, where the adiabatic warming up of the gas becomes noticable.

At a low pressure the phase changes almost linearly with the pressure and the amplitude remains constant. This is the pressure range where the OT detector is especially suitable. The small circles in the Fig. 2 mean the values measured with the design. They follow the theoretical curves with good accuracy for the amplitude as well as for the phase. Thus we can say that (4) is a sufficiently good approximation, and we can use it to evaluate measured data of the OT detector.

3. Measurements of Ammonia $^{14}NH_3$ and $^{15}NH_3$

For the measurement of absorption coefficients by means of an OT detector we shall take its measuring characteristic into consideration. The investigation of $^{14}NH_3$ and $^{15}NH_3$ shall be an example. The ammonia with various nitrogen isotopes has, in the natural gas mixture, the absorption coefficient $\alpha = 2.3 \times 10^{-1}\text{m}^{-1}\text{Pa}^{-1}$ at the $^{13}CO_2$ laser line $R(24)$ and $\alpha = 9.1 \times 10^{-1}\text{m}^{-1}\text{Pa}^{-1}$ at $R(18)$ of the $^{13}CO_2$. For certain applications detection of 1% alterations of the ratios of the concentrations of these two isotopes is needed with great accuracy. This task seems solvable by means of the OT detector because of its low noise equivalent of about $2 \times 10^{-6}\text{W/mHz}^{1/2}$ [2] and because of the nonexisting background signal. $2 \times 10^{-6}\text{W/mHz}^{1/2}$ means that the noise of the electronic device is related to an absorbed power of 2×10^{-6}W on a length of 1m when the measuring bandwith is 1Hz. By using the apparatus described below the dependence of the absorption signal on the total ammonia pressure was measured. (i.g., look at Fig. 3, showing the behaviour of the $^{14}NH_3$ signal). Changes of the total pressure greater than 0.5% could be detected distinctly. This limit was not determined by the noise of the OT detector (we worked with a laser power of 50mW), but by the reading accuracy of the pointer's deflections.

A similar behaviour, however, with greater accuracy because of the greater absorption coefficient has been found for $^{15}NH_3$. The snapping off of the curve at pressures above 1.3×10^2Pa is caused by doing the measurement at a phase optimized for 1.3×10^2Pa. The dependence corrected by means of (4) (small triangles) does not show this snapping off, it is related to the normal absorption curve. This is shown also by the dashed curve, that is reduced by dividing by the total pressure and by multiplying it with 1.3×10^2Pa, and that hints at a noncentral absorption because of its proportionality to the gas pressure.

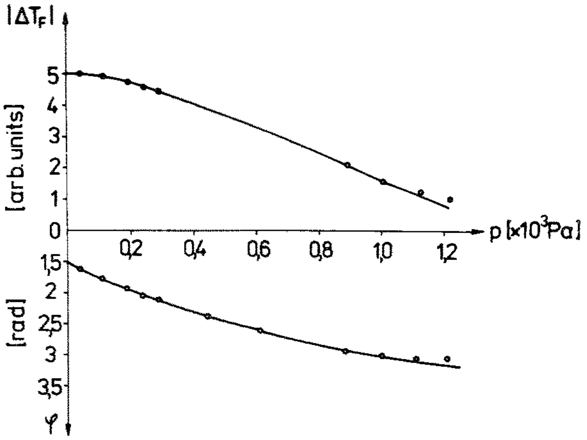

Fig. 2. Amplitude and phase behaviour of the OT detector in the heat diffusion range. —— numerically calculated behaviour, ○○○ experiment

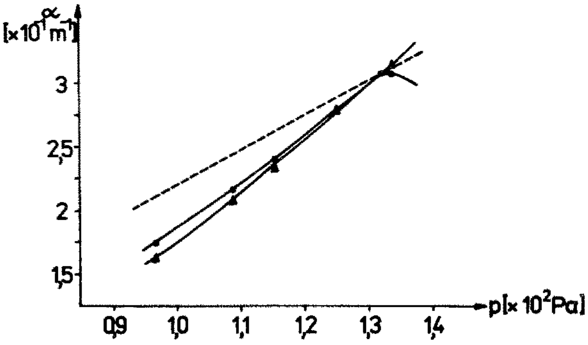

Fig. 3. Absorption behaviour of $^{14}NH_3$. ○○ experimental data without correction, △△ data, corrected by means of (4), – – corrected data divided by $p/1.3 \times 10^2$Pa

An important parameter for quantitative measurements is the reproducibility of measured data. As ammonia is adsorbed by surfaces of the apparatus very strongly, the long-time stability of OT measurements was investigated with water vapour at CO laser wavelengths. A reproducibility better than 1% was obtained with one gas filling for a measurement lasting a week. Finally, we want to point out that the design used for these measurements with $R_2 = 1.1 \times 10^{-2}$m was not optimized to the pressure range around 1.3×10^2Pa, but it was conceived for pressures below 10Pa. This caused the needed relatively strong corrections of the values.

4. The Apparatus

Figure 4 shows the measuring arrangement, being on the whole the same as described in [1, 2]. Thus it shall

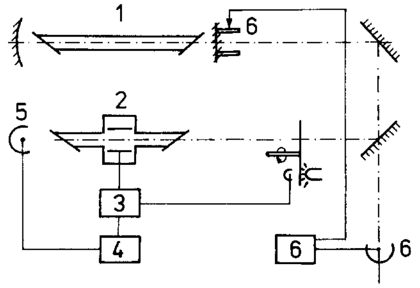

Fig. 4. Experimental arrangement for linear absorption measurement by means of an OT detector (*1* CO_2-laser, *2* OT, *3* lock in amplifier, *4* apparatus dividing the OT signal by the laser power signal, *5* laser power detector, *6* laser frequency stabilizing system)

not be explained here. Only the method for determining the signal magnitude may be mentioned.

The signal S of the OT detector is proportional to the absorption coefficient α of the gas and to the input light power I_F between the pyroelectric foils:

$$S=\alpha I_F K_{\mathrm{OT}}\,. \tag{6}$$

K_{OT} is the factor signifying the sensitivity of the OT detector. The pyroelectric foils are placed in the middle of the detector, that has the length L, so that the light power I_F can be expressed by

$$I_F=I_0\exp(-\alpha L/2)\,. \tag{7}$$

The laser detector 5 in the Fig. 4 provides the signal

$$S_D=I_0\exp(-\alpha L)\,. \tag{8}$$

K_D is the detector sensitivity. By inserting (7) and (8) into (6) and converting the resulting equation we obtain the expression

$$Q=S/S_D=(K_{\mathrm{OT}}/K_D)\cdot\exp(\alpha L/2)\,,$$

describing the dependence of the relationship Q on the absorption coefficient α. By a single experimental determination of the relationship K_{OT}/K_D these apparatus parameters are excluded.

This procedure is reasonable when $|1-\exp(\alpha L/2)|>10^{-2}$. For smaller values of αL Q provides a direct measure for the absorption coefficient.

5. Conclusions

The construction of the OT detector should advantageously be adapted to the measuring task to obtain maximum sensitivity and small dependence on the kind of gas. So R_2 should be chosen large in the range of low pressures, so that the beam radius can possibly be enlarged to reach a great number of molecules and to get small saturation effects. In every case R_2 must fulfil (5). To extend the theory of OT detectors to higher pressures, we shall publish a paper, dealing with a combined theory of thermal conducting and adiabatic processes.

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