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HIGH PRESSURE CELL TO MEASURE THE DEPOLARIZATION RATIO OF THE LIGHT SCATTERED BY GASES

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Résumé. — On présente un appareillage facile à réaliser permettant de mesurer des taux de dépolarisation supérieurs à 10^{-4} . La principale difficulté rencontrée vient de la biréfringence accidentelle. Nous indiquons comment la minimiser par construction mécanique et comment tenir compte de la biréfringence résiduelle par un calcul et des contrôles appropriés.

Abstract. — An easily assembled apparatus permitting the measurement of depolarization ratio higher than 10^{-4} is presented. The major difficulty arises from the depolarization, due to the birefringence of the windows under stress. We explain how to minimize it by mechanical means, and how to deal with the problem of residual birefringence by appropriate calculation and tests.

1. Principle. — The apparatus presented permits measurements under pressures up to 500 bar and temperatures between 25 and 200 °C. A linearly polarized beam from an argon ion laser passes through a cell containing the high pressure gas. Then the light, scattered at 90°, is analyzed. The plane of scattering is horizontal. By means of a half-wave plate, the polarization of the incident beam is horizontally (h) or vertically (v) oriented. We measure a polarized intensity V_v and three depolarized intensities H_h , H_v , V_h ; H and V indicating the polarization of the scattered beam.

Away from the critical point, the three depolarized intensities are equal and inferior to V_v . The depolarization (η) is defined by the ratio of one of the depolarized intensities to V_v . Three difficulties arose :

- a) The birefringence of the stressed windows under pressure;
 - b) The parasitic light and;
 - c) The poor geometrical definition of the scattered beam due to the finite apertures of the diaphragms.
- How these problems can be solved is indicated.

The study of the depolarized intensities in the fluids permits a better knowledge of the interactions, the molecular distributions, the thermodynamic properties of the fluids (see examples [1] to [7]) and of the collision induced anisotropy ([4], [8]).

2. Apparatus. — The cell of KNDMO steel (Fig. 1) is formed of 4 perpendicular branches containing diaphragms which minimize the parasitic light due to the reflection on the edges of the cell, and limit the aperture of beam on the photomultiplier's side.

The windows are cylinders of tempered PUROP-

FIG. 1. — (1) high pressure cell, (2) analysing polaroids, (3) iris diaphragm, (4) photomultiplier, (5) incident beam, (6) density plate, (7) half wave plate, (8) glazebrook, (9) half wave plate, (10) laser.

SIL. A which presents a small birefringence under stress. The residual depolarization, which cannot be minimized easily will depend essentially on the pressure and mechanical bearings (Fig. 2) of the window in its mounting screwed to the cell. The use of steel

FIG. 2. — (1) hold-down nut, (2) polished cylinder (KNDMO-steel), (3) window (PUOPSIL A), (4) QUINSON ring - DN 20, (5) QUINSON ring - DN 4.

polished cylinders, causes a better distribution of the stress. The gas tightness is achieved by means of QUINSON rings. The apparatus must be carefully assembled and stabilized for full reliability of the measurements. The main difficulty is to obtain a good polarization of the incident beam. The horizontal polarization must be accurately realized; the fine control of the latter is obtained by detecting a minimum of V_h with the P.M. A slight vertical component will entail an important increase of the detected signal. A retractable system supporting a half-wave plate gives the vertical polarization whose adjustment is less critical.

On the scattering side, H_h must be separated from V_h , and V_v from H_v , according to incident beam polarization. V_v is 10^3 times bigger than the three depolarized components which are all equal. So, it's not necessary to use a high quality polarizing prism, and the use of polaroid, the adjustment of which is not critical in this case, gives the same kind of results as those obtained by a glazebrook for instance. We have chosen the polaroids because their size allows their setting in revolving systems. The difficulty lies in the reproducible setting of pre-adjusted polaroids. The pre-adjustment of the horizontal positioning of a most critical setting is made by detecting a minimum of H_v with the P.M. A light-tight revolving mechanism is used.

To make measurements at different temperatures, a heating-plate was placed against the cell; the temperature is stabilized at $1/10^\circ\text{C}$. It must be heated progressively to avoid extra stress on the windows.

The cell is isolated from its support by quartz-balls. The cooled P.M. being thermally protected by brass-bellows.

3. Experimental difficulties. — The main difficulty is to maintain the polarization of the incident and scattered beams, when they cross the windows of

the high pressure cell. Special care must be given to the fitting of the window-holders. Besides, simultaneous measurements of H_h , V_h , H_v control the depolarization of the stressed windows, by comparing the values of the depolarized components that must be equal, when there is no stress. We have indicated how to take into account those depolarizations when they're small, to obtain the exact value of the depolarization ratio.

η is defined as being H_h/V_v or V_h/V_v or H_v/V_v when there's no windows' depolarization. Let β be the depolarization ratio introduced through the entrance window on the incident beam, β' the one introduced on the scattering side, V_v the intensity of V_v if β and β' were nil; we can establish the following identities:

$$\begin{aligned} H_h &= \eta + \eta\beta + \eta\beta' + \beta\beta' \\ H_v &= \eta + \beta' + \eta\beta' + \eta\beta\beta' \\ V_h &= \eta + \beta + \eta\beta' + \eta\beta\beta' \\ V_v &= 1 + \eta\beta + \eta\beta' + \eta\beta\beta' \end{aligned} \quad (1)$$

The intensity unit being: $V_v/(1 + \beta)(1 + \beta')$.

In the range of pressure that were used, the values of β and β' have reached 10^{-3} . The measurements of H_v/V_v and V_h/V_v are disturbed, while H_h/V_v is less affected, as shown in (1). So we decided to devote our study to the ratio H_h/V_v essentially, taking the effect of window depolarization into account on using the experimental values of H_v/V_v and V_h/V_v .

From (1) a good approximation of η is derived which allows the control of the parasitic depolarization.

$$\eta = \frac{H_h}{V_v} - \frac{H_v \cdot V_h - (H_h)^2}{(V_v)^2} \quad (2)$$

Yet another experimental difficulty is encountered when collecting the scattered light since infinitely small diaphragms cannot be used, and we no longer operate at a rigorous 90° of the incident beam which confuses the intensities H_h , V_h and V_v . This confusion adds supplementary constants ($\sim 0.5 \times 10^{-3}$) to the ratios H_h/V_v and V_h/V_v [5]. Those constants are related to the solid angle of the scattered beam; they don't disturb the study of the variation of *versus* the density of the gases, but, they must be subtracted for absolute measurements.

In theory, the depolarization ratio, that is proportional to the number of atoms, must be null at the origin of the pressures. The constants are obtained by measuring the depolarization ratio of argon under zero pressure, by extrapolating the curves. The optimal inclination of the rays can be obtained by means of lenses L_1 and L_2 while sufficient luminosity is maintained. The iris-diaphragm D is at the focus of the system L_1 and L_2 ; the inclination of the scattered rays detected by the P.M. can be diminished by closing the iris-diaphragm. The bearing of the window which is at the L_1 focus plays the role of a dia-

phragm. So, all the selected rays may come from the whole surface of L_1 .

The parasitic light disturbs the measurement of Hh too: it is mainly due to the reflections coming from the incident beam and the corresponding intensity is approximately $2 \times 10^{-3} \times Vv$ of argon under atmospheric pressure. Such a low value can be obtained by means of a carefully chosen set of diaphragms.

4. Measurement analysis. — Hh , Vh , Hv and Vv are measured at different temperatures and under different pressures. Then, Vh and Hv are compared with Hh , thus the evolution of β and β' can be plotted.

By extrapolating the graphs Hh and Vv at the origin, we deduce the contributions due to the parasitic light, which allows for the corrections of Hh and Vv and the calculation of η . The original value η_0 deduced from the graph of η versus pressure P , for an isotropic gas, without Raman spectrum such as argon, is the depolarization ratio due to the finite aperture of diaphragms. This constant value must be deduced from all the values of $\eta(P)$ for all isotropic and anisotropic gases.

Even under moderate pressures, errors in the measurement of the depolarized components can be introduced by accidental depolarizations; but its effects can be limited, by using good window bearing. It's shown by graph 1: experiments (A) and (B)

GRAPH 1. — Effect of the window bearing quality upon the depolarized intensities.

have been made in the same pressure range and temperature. In the second series of experiments (B) an improvement of the planicity of the polished bearing, considerably reduced the windows' depolarization, so that no correction was necessary to calculate η . It can be observed that in the (A) experiment the value of Vh is extremely high, as compared with the real Vh value practically observed in the (B) experiment. In (B), the values of Hh and Vh are similar. The graph 1 shows that the stress induced depolarization of window perturbs more Vh than Hh ; it's in agreement with (1).

The correction (2) permits practically to calculate η even in experiment (A) up to a pressure of 200 bar. In experiment (B), η is practically equal to Hh/Vv , no correction is necessary. Nevertheless correction (2) can be very useful if quality of bearing is not exceptional.

The experiments, shown in graph 1, have been made with methane which presents no depolarization under zero pressure, when the Raman spectrum is suppressed by an interferential filter in front of the P.M. It can be noted that the extrapolated value under low pressure:

$\eta_0 = 0.5 \times (10^{-3})$ corresponds to that obtained with argon in a similar experiment: it's due to the finite diaphragms' aperture which is an apparatus characteristic. As previously said, we reported the values $\eta - \eta_0$ on graph 2 and 3.

GRAPH 2. — Depolarization ratio versus pressure for isotropic gases.

GRAPH 3. — Depolarization ratio versus pressure for anisotropic gases.

Our measurements have been made in a range of 0 to 400 bars with isotropic gases (Ar and CH_4) and anisotropic gases (N_2 and C_2H_6). Similar results have been commented (4) and (9). An collision induced anisotropy effect augmented with an aniso-

tropic effect proper I_p to all anisotropic molecules could thus be brought into evidence.

5. Conclusion. — We have described a mechanism permitting the reproducible study of depolarization of the light scattered by isotropic or anisotropic molecules.

Depolarization ratio up to 500 bar can be measured
a) by the minimization of stressed windows' birefringence and the corrections made to take it into account,

b) by limiting the inclination of the scattered rays,
c) by reducing the parasitic light by an adequate set of diaphragms.

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