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THE ACOUSTIC PROPERTIES OF METHANE HYDRATE

By

BRILLOUIN   SPECTROSCOPY

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Abstract

The report describes the second phase of investigations of the acoustic properties of methane hydrate by Brillouin spectrocopy. Very importantly it concludes that the p-wave velocity of the structure 1 hydrate is 7% lower than for ice, thus confirming some earlier theoretical work.

Résumé

Ce rapport décrit la deuxième étape de la recherche sur les propriétés acoustiques de l'hydrate de méthane utilisant la spectroscopie Brillouin. Sa conclusion importante est que la vitesse des ondes longitudinales de l'hydrate du type 'structure 1' est de 7% inférieure à celle de la glace. Les résultats de quelques études théoriques antérieures sont ainsi confirmés.

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A report

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The purpose of this continuing project is to determine the acoustic properties of pure methane hydrate utilizing the method of Brillouin spectroscopy, with a determination of the acoustic velocity as the immediate objective. This information is of value if seismic techniques are to be applied to the problem of detecting methane hydrate in the natural environment (in the ocean sediments and particularly under the permafrost regions of Canada and the USSR). At present there is no reliable method of detecting in situ hydrate.

As described in previous reports (Dec. 8, 1979 and April 15, 1980), Brillouin spectroscopy involves the scattering of light by the ambient, thermally-induced elastic waves in a given material. The associated Doppler shift in the scattered light can be accurately measured by Fabry-Perot interferometry, and this shift is proportional to the acoustic velocity. The technique can be employed with very small samples or thin films (of dimensions less than 0.1 mm) provided that the optical quality, or clarity, is acceptable, and provides definite advantages in the case of difficult-to-produce materials such as methane hydrate. The problem of optical quality is, however, a difficult one in this particular case.

Experimental Apparatus and Procedures

In the report of April 15, 1980 methods and apparatus were described for successfully obtaining bulk samples (of a few mm^3 volume) of methane hydrate. In brief, a continuous flow of methane gas at about 700 psi pressure was maintained through a

reservoir of water (Fig. 1) and the resulting gas mixture was delivered via a vertically adjustable hypodermic tube (0.5 mm o.d.) to the bottom of a thermoelectrically cooled quartz sample tube (1.5 mm i.d., 6.5 mm o.d.). A highly polished quartz plug was cemented in the bottom of the sample tube to provide for laser beam entry (Fig. 2). It was possible to initiate growth on the surface of the bottom window and, by slowly adjusting the position of the hypodermic tube, a bulk sample of methane hydrate was grown vertically up the sample tube.

During the past year, and with the exception of periodic methane leakage problems, this equipment has been working well. Several bulk samples were produced and were initially considered usable for light scattering purposes since they appeared relatively clear under visual observation. However, when the focused laser beam was introduced into the sample a very intense diffuse scattering was observed. Several unsuccessful attempts were made to obtain the Brillouin spectrum using the photon counting system as previously described in the report of Dec. 8, 1979 (see also Fig. 3). Possible indications of a spectrum were observed near the bottom of the cell, but it was apparent that the intense parasitic scattering (at the laser frequency) was inhibiting the penetration of the laser beam into the sample in a spatially well-defined manner. Multiple scattering of light at the Brillouin frequencies may have been troublesome as well, and consequent efforts were made to observe the scattered light at the laser beam entry point, i.e. at the very bottom of the cell, while at the same time adjusting this entry point to lie as closely as possible to the cell wall. These

efforts were, in turn, unsuccessful due to the presence of a ring of epoxy cement which extended slightly up the cell wall from the surface of the quartz plug.

A modification of the sample preparation method was undertaken at this point so that the desired conditions (above) could be more closely approached. The new preparation method was in fact closely related to the original procedure as described in the report of Dec. 8, 1979. Namely, a clear crystal of ice about 2 mm high was first grown in the sample cell, and a very thin layer of hydrate was then formed on the surface of the ice at about 0 $^\circ$C by pressurizing the cell with 800 psi of methane via the back-fill valve of Fig. 1. This process usually lasted a few days, after which the sample was cooled to -16 $^\circ$C to render it more resistant to melting or deterioration upon introduction of the laser beam. The incident laser light could now be observed to pass through the ice as a narrow, clean, and well-focussed beam before encountering the hydrate layer. Although the previously mentioned epoxy ring (at the bottom of the cell) still presented a problem, it was nevertheless possible to bring the laser beam closer to the cell wall at the 2 mm height and, with further adjustments to the external optics as described below, unambiguous spectra of the hydrate were eventually obtained.

It should be noted here that the alternative, and perhaps more procedurally correct, approach of redesigning the cell was considered as a solution to these problems. However, it was decided that this approach would be less likely to achieve success within the time constraints of the contractual committment.

The parasitic scattering from the hydrate layer was still very intense but, at the same time, efforts to discriminate against it were more successful because more precise alignment and optimization of the scattering optics was now possible via observation of the Brillouin spectrum of ice just below the hydrate layer. A quartz plate of 2 mm thickness (situated at P in Fig. 3) was now slowly rotated so that the scattering volume being observed was gradually adjusted upwards into the hydrate layer and, after several days of continuous data acquisition, a spectrum of the hydrate became evident. It was also apparent that the quality of the spectrum could be further enhanced by a more thorough rejection of the substantial level of superfluous radiation which was still being detected.

Toward this end the photomultiplier detector was fitted with additional baffles so as to more severely restrict its field of view. It was also equipped with a 100 Angstrom band-pass filter centered at the laser wavelength which served to effectively reject Raman radiation from the sample as well as broadband ambient radiation from instrumentation within the room. In addition a spatial filter was introduced between lens L_1 and the Fabry-Perot interferometer. This device effectively achieves a more precise definition of the scattering volume and involves the focussing of the scattered light through a small diameter (0.1 mm) pinhole before transmission to the interferometer. The price that is paid takes the form of a much higher degree of precision in the optical alignment which in this particular case was very difficult to achieve. Nevertheless

these measures were considered well worthwhile since they had
the desired effect of improving the quality of the spectra to a
level of acceptability.

Results

A reproduction of a methane hydrate spectrum is shown in
Fig. 4. The spectrum represents five days of accumulation time
at a laser power of 50 mW. The hydrate peaks h' and h" correspond
to intensity levels of less than 1 photon count for every 10
seconds of accumulation time, with the background radiation
arising almost entirely from the dark count of the photomultiplier
tube. The intensity level at the laser peaks (R' and R") was
typically a million times higher than at the hydrate peaks.

The spectral features h' and h" are associated respect-
ively with receding and approaching longitudinal acoustic waves
in methane hydrate and the identical Doppler shifts (between
R' and h', and between R" and h") were determined to be (ν_s=) 12.8
GHz. Recalling the Brillouin equation as discussed in the report
of Dec. 8, 1979, the observed Doppler shift is related to the
acoustic velocity (v) in accordance with

$$\nu_s = 2\nu_0 (v/c)nSin(\alpha/2) \qquad (i)$$

where ν_0 is the frequency of the incident laser light, c is the
velocity of light in vacuum, n is the index of refraction of the
scattering medium (methane hydrate), and $\alpha=90^0$ is the scattering

angle. The value of n was calculated via the Lorentz-Lorenz
relation

$$L\rho = (n^2 - 1)/(n^2 + 2) \qquad (ii)$$

where ρ is the density. The constant L was determined from the
known values of n (=1.312) and ρ (=0.9164 g cm^{-3}) for ice at -16 ^{o}C.
Since the structure of the hydrate lattice is known the density
could be calculated for the limiting cases of empty cages
(ρ = 0.790 g cm^{-3}) and completely filled cages (ρ = 0.9121 g cm^{-3}).
* Assuming 93% occupancy of the cages to apply in practice (Galloway,
1970) a hydrate density of 0.9049 g cm^{-3} was then obtained by
linear interpolation. Substitution of this value in equation (ii)
then yielded n = 1.31 and, when used together with the measured
Brillouin shift in equation (i), resulted in a value of v = 3560 m s^{-1}
for methane hydrate at -16 ^{o}C. This is to be compared with the
corresponding value of 3845 m s^{-1} for ice and represents a ratio
of 0.93 ± 0.01 . This result, which should be regarded as prelim-
inary, was presented at the Fourth Canadian Permafrost Conference
(1981) in Calgary, Alberta. It agrees well with the ratio of
0.939 as calculated by Whalley (1980) for the full structure I
hydrate, but is not in good agreement with the measured value of
0.837 for propane hydrate I (Pandit and King, 1981). This latter
discrepancy could, however, be correlated with the different
techniques of velocity measurement and sample preparation which
were employed in the two experiments.

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* variation of the cage occupancy by several percentage points does
not significantly affect the resulting value of n.
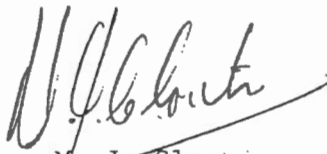
Conclusions

It is felt that, although the difficulties are considerable, the preceding results adequately demonstrate the viability of applying Brillouin scattering techniques to the study of acoustic properties in the case of methane hydrate. Reasonable objectives for continued work in this area should include (1) improvements in the accuracy of the preliminary results presented above, (2) determination of hypersonic attenuation through Brillouin line-width measurements, and, (3) detection and measurement of the (much weaker) shear-wave components of the spectrum which, by comparison with ice, could provide more discriminating information vis à vis the detection of methane hydrate in the natural environment.

It is reasonably clear, however, that the successful realization of these objectives will depend in an important way on the degree of success attained in the preparation of higher quality samples. Because of the particular complications (mainly associated with the high pressure requirements) which arise in the case of methane hydrate, it would undoubtedly be of value at this stage in the investigations to temporarily divert the focus of attention to a more experimentally tractable case such as the hydrate of tetrahydrofuran or of xenon. This would more readily permit the systematic investigation of correlations between the conditions of hydrate formation and the quality of the resulting samples.

Progress in this project has been impeded to a considerable degree by the need to rely on the use of equipment which is

committed on a priority basis to other experiments in this
laboratory. This point will be further addressed in the accompany-
ing continuation proposal.

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References

T. J. Galloway et al   1970   Ind. Eng. Chem. Fundam. $\underline{9}$, 237

B. I. Pandit and M. S. King   1981   Fourth Canadian Permafrost
Conference, Calgary, Alberta

E. Whalley   1980   J. Geoph. Res. $\underline{85}$, 2539

Figure Captions

Fig. 1   Schematic drawing of the high pressure gas handling
         system.

Fig. 2   Details of the sample region.

Fig. 3   Overall arrangement of apparatus in the Brillouin
         scattering experiment: L - lens, M - mirror,
         A - aperture, S - sample site, P - rotatable quartz
         refracting plate, PM - photomultiplier tube,
         AD - amplifier discriminator, DAS - data acquisition
         and stabilization system.

Fig. 4   Reproduction of a Brillouin spectrum of methane
         hydrate. The features labeled R arise primarily
         from parasitic scattering at the incident laser
         frequency. The labels i and h identify the longit-
         udinal components of ice and methane hydrate, respect-
         ively. The sweep rate was programmed to increase the
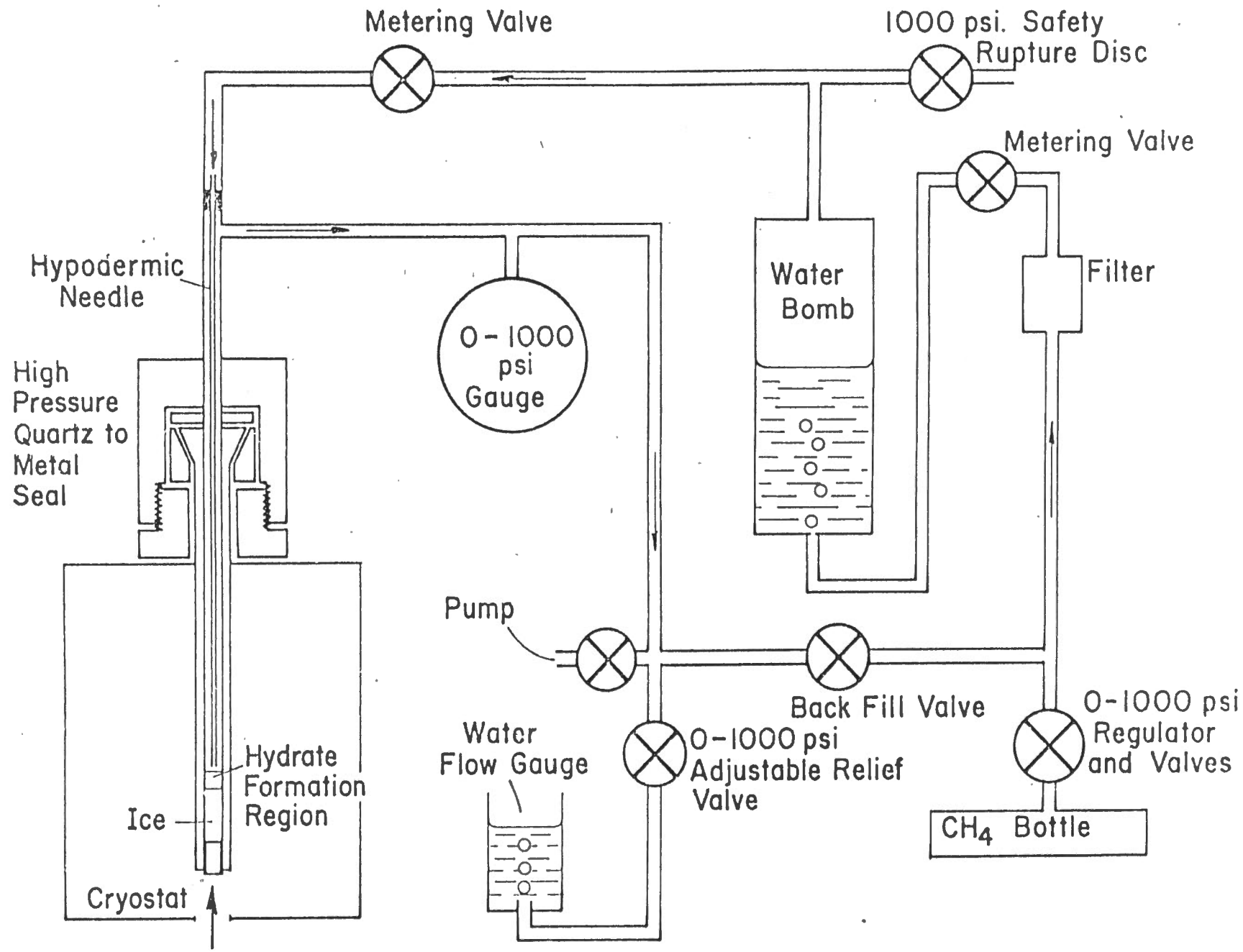   time spent in the region of interest by a factor of 80.
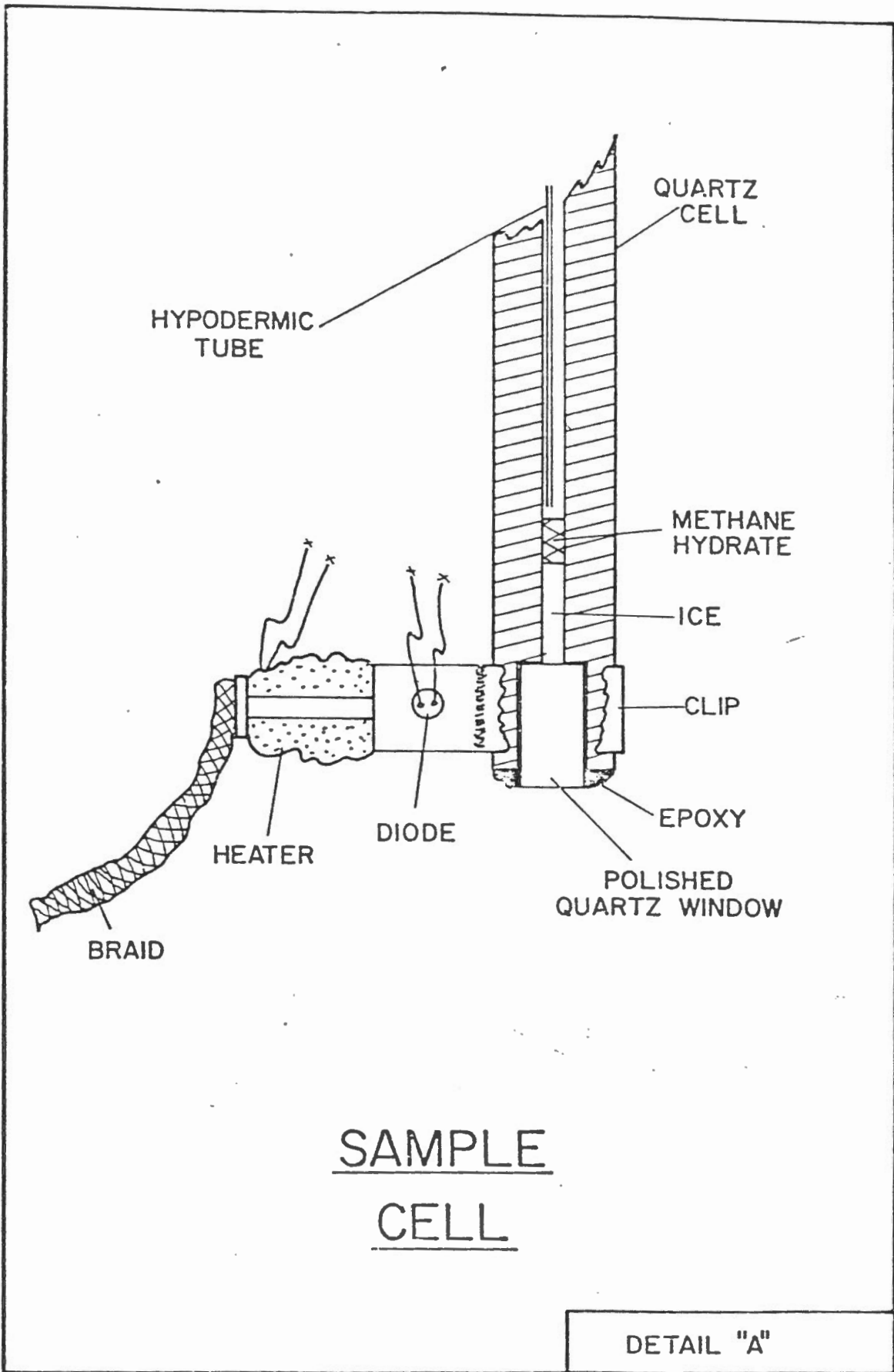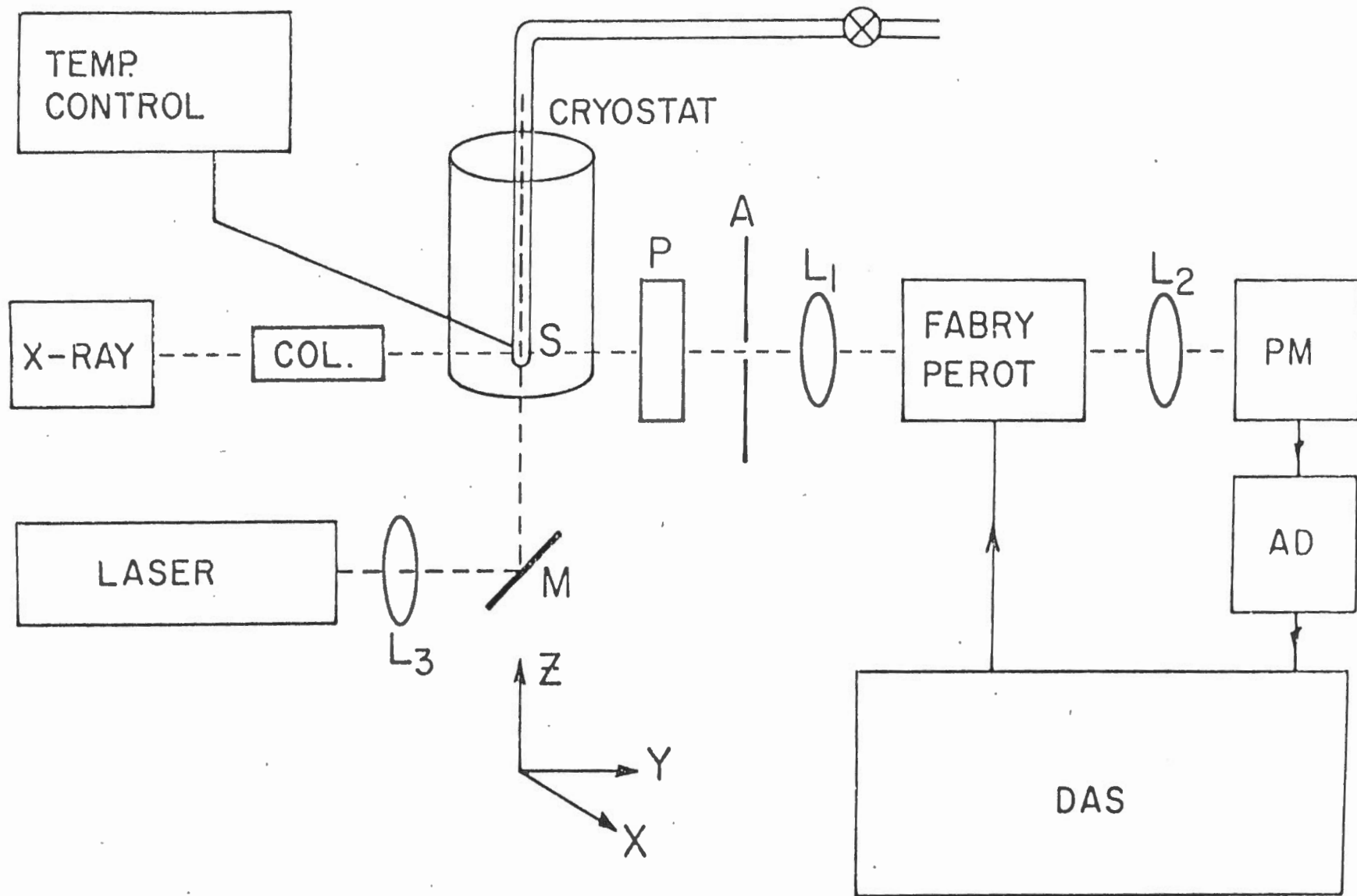
FIGURE 1

QUARTZ
CELL

HYPODERMIC
TUBE

METHANE
HYDRATE

ICE

CLIP

EPOXY

DIODE

HEATER

POLISHED
QUARTZ WINDOW

BRAID

SAMPLE
CELL

DETAIL "A"

FIGURE 2

FIGURE 3

FIGURE 4