spectrovision

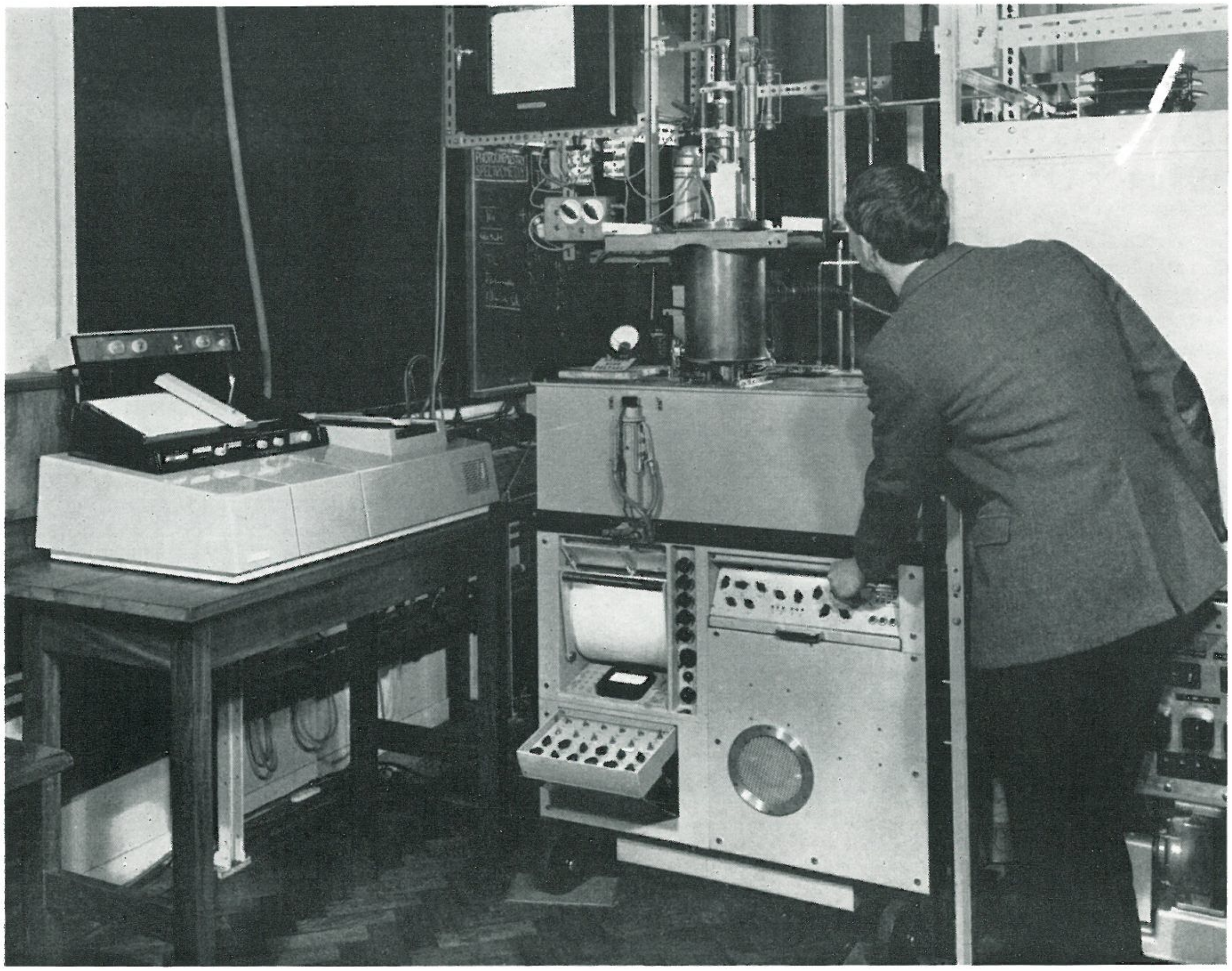
Number 16, 1966

Published by: UNICAM Instruments Ltd., Cambridge, England. Tel: Cambridge 61631

UNICAM

THE QUEEN'S AWARD
TO INDUSTRY 1966

Contents



Infra-red Spectroscopy, Cryogenics and Photochemistry

J. F. Ogilvie, Ph.D (Cantab.) (Department of Physical Chemistry, University of Cambridge)

Introduction

Occasionally, when two techniques that have been developed separately are combined, the resulting combination makes possible studies which are not simply an extension of either technique. An instance is furnished by cryogenics and infra-red absorption spectroscopy, development of both of which was initiated about the turn of the century. Thus Dewar attained temperatures below 100°K in liquefying oxygen, nitrogen and hydrogen, and also conducted chemical reactions at the temperatures provided by these refrigerants. Coblentz developed infra-red spectroscopy and recognized the potential importance of this technique for the analysis of stable molecules. When these physical methods were combined, starting about 1953, there arose the possibility of the direct detection of radical intermediates—molecular fragments—because the radicals could be trapped in an inert, transparent, solid solvent for the period of hours required to permit spectrophotometric observations of their characteristic absorption bands. This article outlines some of the techniques practised in the author's laboratory and some results are presented for illustrative purposes. Photochemical methods of generating certain trapped radicals are particularly convenient, and have consequently been usually employed.

Instrumentation

THE CRYOSTAT

The principal apparatus required for this research work is an optical cryostat. A particularly useful design is that of Deurig and Mador[1], shown in figure 1. In the very low temperature region, the thermal conductivity properties of materials are especially worth considering. In Table 1 are presented thermal conductivity data of argon, caesium iodide, copper, and inconel alloy (slightly preferred to stainless steel), for temperatures mostly in the cryogenic range. These four substances are fairly representative of molecular solids, crystalline dielectrics, pure metals and disordered alloys respectively.

Thus in the cryostat used in this laboratory, copper or inconel was employed as the constructional material where good or bad thermal conductivity respectively was desired; otherwise brass was used, but all cooled brass and copper surfaces were copper-plated and polished well to reduce emissivity. The single cooled window in this cryostat is a thin crystal of caesium bromide, whose thermal conductivity may be assumed to be similar to caesium iodide and which is optically transparent from the far ultra-violet (50,000 cm^{-1}) to the far infra-red (200 cm^{-1}). Because of its non-close-packed lattice structure it is not susceptible to thermal shock. Although caesium bromide has good thermal conductivity at very low temperatures, its coefficient of thermal expansion is, in common with other alkali halides, approximately twice that of many metals useful as construction materials, and this gives rise to problems of thermal contact between window and supporting block at low temperatures.

It is obvious from the data in the table that an optimum temperature for operation is near 7°K. Argon, a transparent, absolutely chemically inert, rigid solvent, has at that temperature a thermal conductivity (for annealed samples) just less than its maximum value. However the insignificantly small vapour pressure of argon at that temperature, desirable for the attainment of good isolation in the dilute matrix frozen slowly from the gas phase, causes to form a microcrystalline deposit which strongly scatters incident radiation. Liquid helium at its normal boiling point 4°K conveniently acts as a refrigerant for this temperature region.

TABLE 1

Thermal conductivity data (units of watts-cm^{-1} $degree^{-1}$) for various annealed solids

Temperature	Ar	CsI	Cu	Inconel
4°K	20×10^{-3}	1·0	120	3×10^{-3}
7	35	1·8	130	6
10	44	0·9	140	10
20	14	0·2	105	20
50	5	0·09	10	50
100		0·05	6	90
300		0·01	4	150
Reference	2	3	2	2

The liquid helium compartment of the present cryostat has a capacity of $1\frac{1}{2}$ litres, and requires $3 \pm \frac{1}{2}$ litres of liquid helium for cooling (from 77°K) and filling. A single charging with liquid helium usually allows a working period of approximately 12 hours, but has lasted 26 hours on occasion. If alternatively nitrogen were employed as a refrigerant, the pumping away of vapours from the liquid and, eventually, the solid would reduce the temperature to 45°K, and this could be maintained for at least a week. The radiation shield can hold 2 litres of liquid nitrogen which last 17 hours per filling. The lower portion of this cryostat is shown in figure 2. Coming down from the brass flange at the top of the photograph are two glass tubes, ending near a port in the radiation shield, which lead the gaseous samples from storage bulbs to the caesium bromide crystal. At the bottom of the radiation shield, the rotating shroud, which prevents unnecessary heat input from ambient

COVER PHOTOGRAPH

Photograph of the optical cryostat mounted in the SP100 infra-red spectrometer in the author's laboratory.

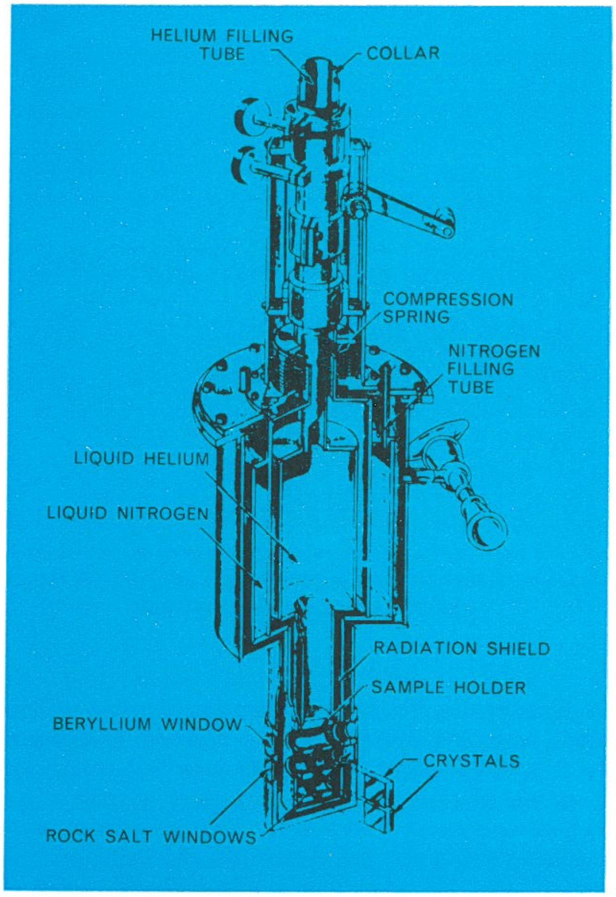


Fig. 1. Cutaway drawing of the optical cryostat designed by Deurig and Mador, taken from reference 1.

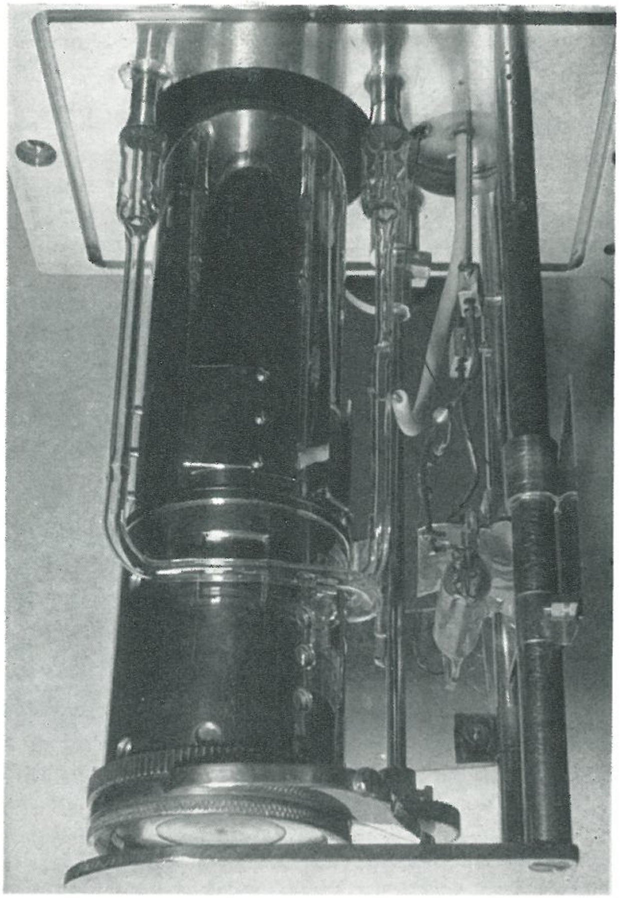


Fig. 2. Photograph of the lower portion of the author's cryostat, usually mounted within the SP100 cell well.

temperature sources to the liquid helium vessel through apertures in the radiation shield not actually in use, is actuated by the gear mechanism visible above the base plate. A primitive low-pressure mercury lamp, supported from the flange by its electrical leads, is opposite the port for deposition near the glass jets.

THE SPECTROPHOTOMETER

As shown in the photograph (on page 1), this cryostat is designed to be operated in the Unicam SP100 Double-beam Infra-red Spectrophotometer[4]. At the top of figure 2 can be seen the groove for the O-ring in the flange which adapts the cryostat to the spectrometer cell well. The sample beam passes through the caesium bromide window (on which sample gases are frozen) and appropriate ports of the cryostat and under the mercury lamp on its path through the spectrophotometer. The Unicam spectrophotometer has two distinct advantages in having a totally evacuable optical path: thus there can be no air leakage through the potassium bromide window seals of the cell well, and therefore no atmospheric absorption of measured infra-red radiation. Also, adapting the cryostat to the cell well means that only one extra window is placed in the sample beam.

The wide range and grating resolution of the SP100 spectrophotometer are desirable for the narrow absorption bands of solids at low temperatures. The 8-micron grating is used in the third order[5] as well as the first, to increase the grating range to 5000 cm^{-1}, and an additional slit programme has been prepared and fitted for use in this new grating range. A commercially made multilayer transmission filter of tellurium and thallous chloride has been mounted after the exit slit of the prism monochromator, and is actuated manually by a loose coupling mechanism through the lid of the monochromator casing. Replacing the inefficient polyethylene scatter filter, this new filter for the potassium bromide prism range reduces false radiation to an amount not detectable at 375 cm^{-1}. Hence one can scan from 370 to 5000 cm^{-1} with spectral slit widths usually less than 4 cm^{-1} at conveniently rapid scanning speeds.

Although the standard spectrometer thus serves well for spectroscopic functions, the restricted access to the sample in the cell well presents difficulties in photochemical experiments. Several modifications have been effected to increase the utility of the SP100 instrument for our investigations. The most important of these was to position the Nernst glower source outside the monochromator casing (where it is situated on later models) so that it can be quickly and easily replaced by a Philips HPK 125-watt mercury lamp in a special mounting.

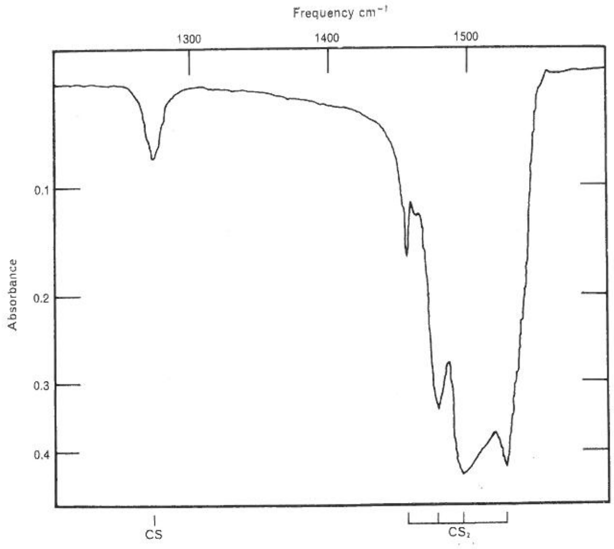


Fig. 3. *Absorption spectrum from* 1200 *cm*$^{-1}$ *to* 1600 *cm*$^{-1}$ *of the products condensed at* 45°*K from a discharge in flowing gaseous carbon disulphide.*

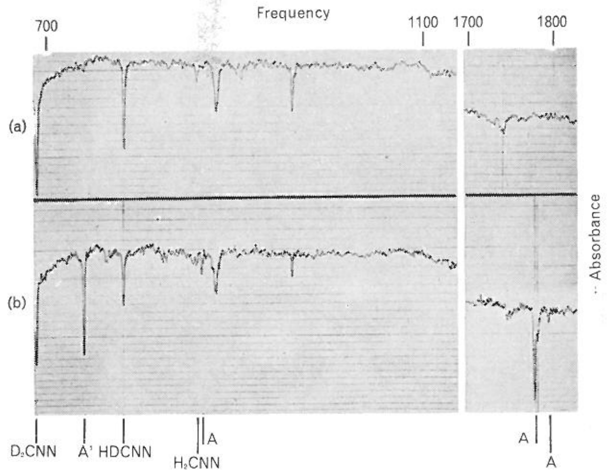


Fig. 4. *Absorption spectra from* 670 *to* 1150 cm^{-1} *and* 1700 *to* 1820 *cm*$^{-1}$ *of diazomethane and decomposition products in an argon matrix at* 4°*K, before (a) and after (b) irradiation with a low-pressure mercury lamp.*

Typical Investigations

The first example of results obtained with this apparatus is the only one not of photochemical generation; the experiment was performed as the first test of this apparatus and is mentioned here for its historical interest. In 1910, Sir James Dewar, Jacksonian Professor of Natural Philosophy in the University of Cambridge, was responsible for the first attempt to trap unstable species from the gas phase. Carbon disulphide vapour was passed through an electric discharge, and the products were frozen in a liquid air trap. The deposit usually exploded violently during the warm-up period when the refrigerant was removed from the trap. The cause of this behaviour was considered to be the diatomic molecule CS. A similar experiment has been performed with solid nitrogen at 50°K as the refrigerant in the cryostat and an induction coil leak tester discharge in flowing carbon disulphide vapour. The spectrum in figure 3 shows the infra-red absorption from 1200 to 1600 cm^{-1} of a thin film of the products after the discharge was employed; a previous scan of the same region after deposition without the discharge operating showed only the (less intense) carbon disulphide around 1500 cm^{-1}. The band at 1259cm^{-1} can be assigned to CS by comparison with the fundamental frequency of 1272 cm^{-1} determined from electronic spectra in the gas phase. This band disappeared completely on standing for 36 hours at 77°K, indicating the reactive nature of carbon monosulphide.

The equipment was used to investigate the photochemical decomposition of diazomethane in an argon matrix near 4°K, the ratio of argon to total diazomethane content being 250. Actually a mixture of isotopic diazomethanes was present, estimated to be 55% D_2CNN, 37% HDCNN and the remainder H_2CNN from the intensities of absorption bands of these parent molecules, as shown in figure 4a. A low-pressure mercury lamp, slightly more efficient than that shown in figure 2 but basically similar, was used for photolysis. After operation of this lamp for three hours, the spectrum shown in figure 4b was recorded. The diazomethane bands are seen to decrease in intensity, whereas weak bands due to impurities are unchanged. Four new absorption lines have appeared, marked A and A′. Those marked A are seen in other experiments when only H_2CNN is present. On the other hand the A′ lines appear when the proportion of diazomethane containing hydrogen atoms is much less relative to deuterium content, in similar experiments. Thus there is direct proof that the molecular carrier of the A and A′ absorption lines contains one and only one hydrogen (or deuterium) atom. This new spectrum has after additional analysis been assigned to the diazomethyl radical, HCNN or DCNN. The value of isotopic substitution in the assignment of absorption bands is hereby illustrated. Complete proof of the assignment would be furnished by spectra of carbon-13 and nitrogen-15 substituted species, which would probably define the number and order of heavy atoms in the structure of this radical.

The last example illustrates that products other than trapped radicals will, if possible, predominate as carriers of the infra-red absorption spectra, even though electron spin resonance data indicate the presence of radicals. This discrepancy arises through the difference in sensitivity and detectivity of the two methods. Radicals, either formed by secondary reactions or stabilized in processes of escape of photo-dissociation products from the site of production in the inert gas lattice, are detected by e.s.r. even though infra-red spectra show that most of the decomposition of the parent substance is followed by formation of stable molecules, possibly as a result of a disproportionation reaction of radicals initially formed in the dissociation process. An instance is the photolysis of methyl nitrite (matrix ratio of argon to CH_3ONO being 250) near 4°K. E.S.R. spectrometers might detect signals due to CH_3O and NO radicals after photolysis. In our experiment, the low-pressure mercury lamp was again used for irradiation; figure 5 shows infra-red spectra of methyl

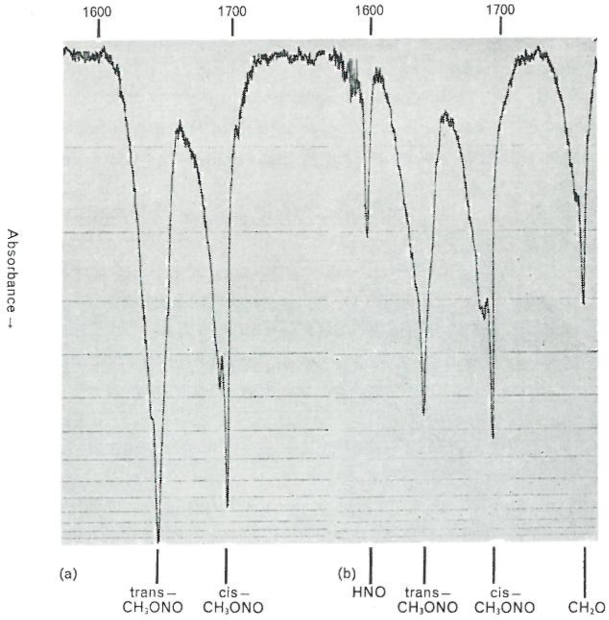


Fig. 5. Absorption spectra from 1550 *to* 1760 *cm*$^{-1}$ *of methyl nitrite and decomposition products in an argon matrix at* 4°*K, before* (*a*) *and after* (*b*) *irradiation with a low-pressure mercury lamp.*

nitrite in the 1600 cm^{-1} region before (5a) and after (5b) photolysis. The absorption of the *trans* rotational isomer of methyl nitrite at 1615 cm^{-1} has decreased more rapidly than that of the *cis* isomer at 1665 cm^{-1}; this effect, not nearly as marked when the Philips high-pressure mercury lamp is used, is being investigated independently. Two product absorptions appear at 1574 and 1734 cm^{-1}, due to nitrosyl hydride and formaldehyde respectively. The former product, HNO, seems stable in the presence of only formaldehyde at temperatures up to 60°K, but it has a lifetime of less than a second in the gas phase at ambient temperatures.

In conclusion, the combination of cryogenic, infra-red spectrometric and photochemical techniques can be understood to constitute a powerful method for determining the vibration frequencies of free radicals and other unusual reactive chemical species.

REFERENCES

1. Deurig, W. H. and Mador, I. L., *Rev. Sci. Instruments*, 1952, **23**, 421.
2. American Institute of Physics Handbook, McGraw-Hill, New York, 1963.
3. Berman, R., private communication.
4. Tarbet, C. S. C. and Daly, E. F., *J. Opt. Soc. Amer.*, 1959, **56**, 603.
5. Ogilvie, J. F., *J. Sci. Instruments*, 1965, **42**, 352.

A method for obtaining isosbestic points on the Unicam SP700 Spectrophotometer

J. Arotsky, B.Sc., Ph.D., M. R. Bramwell and R. M. W. Rickett (*Department of Chemistry, West Ham College of Technology, London*)

Isosbestic points provide useful information for elucidating tautomeric structures and can be used to determine dissociation constants. Comprehensive coverage of the topic is to be found in the literature[1,2,3].

On manual instruments, such as the Unicam SP500 Spectrophotometer, satisfactory results may be obtained, but since readings must be taken at about every 2·5 mμ it is a very time-consuming occupation. To examine just one compound at ten different pH values would require about three hundred readings. On the other hand, flat bed recording instruments like the Unicam SP800 are ideal for the production of superimposed spectra.

To produce isosbestic points on an instrument using a strip chart recorder is not as straightforward as on an instrument with integral flat bed recorder. The method described below, which has been successfully used on the Unicam SP700, is not new, but the finer points described make the method completely reliable. A similar procedure can be adopted for other strip chart recording instruments.

The instrument parameters are selected so that the spectrum is presented in the desired manner on the chart roll. Once this has been done the following procedure is adopted:

1. With the wavenumber marker pens off the paper and the recorder pen to one side, the chart paper is rolled forward so that enough paper is unwound to cover the region of the spectrum to be scanned. The paper is then wound back, the slack being taken up as the paper is rewound. This initial unwinding releases the tension in the paper, which contracts a little as it is unwound.
2. The chart paper is wound forward a little by hand to take up any slack in the recorder, and the recorder pen

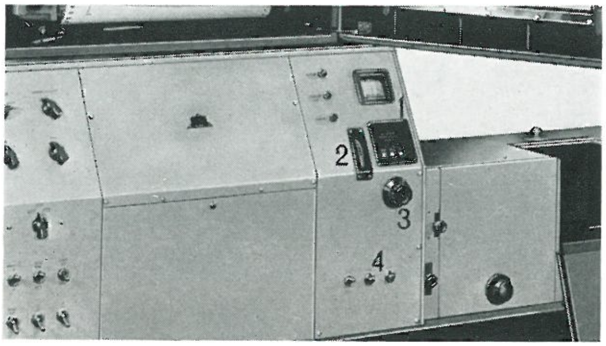


Fig. 1. *Control panel of the Unicam SP*700.