

AN ANALYTICAL TECHNIQUE AS POWERFUL AS THE INFRARED

DISCOVERED experimentally in 1928, and resting on solid theoretical foundations, the spectroscopy of Raman scattering remained for two decades as one of the "finest presents that the physicists had made to the chemists". At a time when the techniques of infrared absorption were accessible only to the very advanced research laboratories, the Raman effect, with its elegant theory of virtually bringing the study of the infrared to the spectroscopy of the visible region, had helped in establishing the structure of thousands of molecules. But the appearance in the market of convenient, automatic, "press-button" infrared spectrophotometers is slowly putting into disuse the Raman spectrographs, and, in fact, these with their conventional mercury burners have the unenviable prospect of figuring more or less as museum pieces only.

However there is no theoretical justification for this disfavour. Infrared and Raman techniques are essentially complementary, and the two together are necessary for establishing the complete spectrum of a molecule. The unique merit of the Raman technique is that it furnishes on a single spectrum information on a wide range of frequencies extending from the very near to the very far off in the infrared.

The reasons for the preference of the absorption methods are not far to seek. They are essentially of a practical nature. Early in the history of Raman spectroscopy accurate measurement of wavelengths of Raman lines was the chief concern of the experimentalists. Now, however, there is the added emphasis on the measurement of their intensities and polarisation which are necessary for a complete understanding of the physics and chemistry of molecules. Any design of a Raman spectrometer should be such as to obtain from it the maximum accurate information that the method itself is theoretically capable of giving. Extensive researches have been done on the requirements of the individual elements,—like the source, the sample cell and its geometry, the monochromator system and its optics, the photomultiplier tubes, the detector and its electronics, etc.,—which go to make up the spectrometer. The main problem designers of Raman spectrometers are confronted with is how to bring in one convenient and reliable set-up all these elements together. The recent discovery of the *Lasers*, sources of light by stimulated emission, has rekindled hope in this field, and one can confidently look forward to

a new era in Raman spectroscopy heralding the renaissance of an analytical technique as powerful as the infrared.

LASER AS RAMAN SOURCE

Lasers with their enormous intensity provide the specialists in Raman spectroscopy the source which is ideally suited to their exacting needs. The conventional monochromatic sources in use previously, namely, mercury tubes at low or medium pressures, produced in the scattering sample only a low density of photons which necessitated the illumination of a great volume of the substance to facilitate any measurement of the Raman effect. On the other hand, the lasers contain in narrow beam a highly augmented density of photons which enables one to excite an intense scattering in a sample of very small volume.

The laser provides other advantages which are no less important. Thus its extreme monochromaticity permits study of spectra of a high degree of resolution. Its parallelism and coherence properties lead to absence of a continuous background and stray parasitic illumination; a higher detectivity is thereby ensured, and observation of scattered rays is possible not only of very weak intensity but also those which are in the immediate vicinity of the exciting radiation. Finally, the high degree of polarisation of the laser beam is a valuable asset for the establishment of molecular symmetries.

PRINCIPLE OF RAMAN SPECTROSCOPY

The Raman effect is the phenomenon of the change of wavelength, accompanied by a partial depolarisation, observed in the scattering of light by molecules or by crystals. In order to study this phenomenon a transparent and homogeneous substance is illuminated by a beam of intense monochromatic light of frequency ν_0 . The analysis of the scattered light by a suitable spectrometer shows, in addition to the exciting radiation (Rayleigh effect), radiations of feeble intensity of frequencies $\nu_0 + \nu_1$, $\nu_0 + \nu_2$, ..., $\nu_0 + \nu_n$... (anti Stokes' rays), and $\nu_0 - \nu_1$ (Raman rays), constituting the Raman spectrum "characteristic of the scattering substance". The values of ν_1 , ν_2 , ..., ν_n ..., which are independent of the exciting radiation ν_0 , are frequencies generally belonging to the rotation spectrum or the vibration spectrum of the molecule.

The "active" frequencies in the Raman effect correspond to movements which are accompanied by a change of the molecular polarisation,

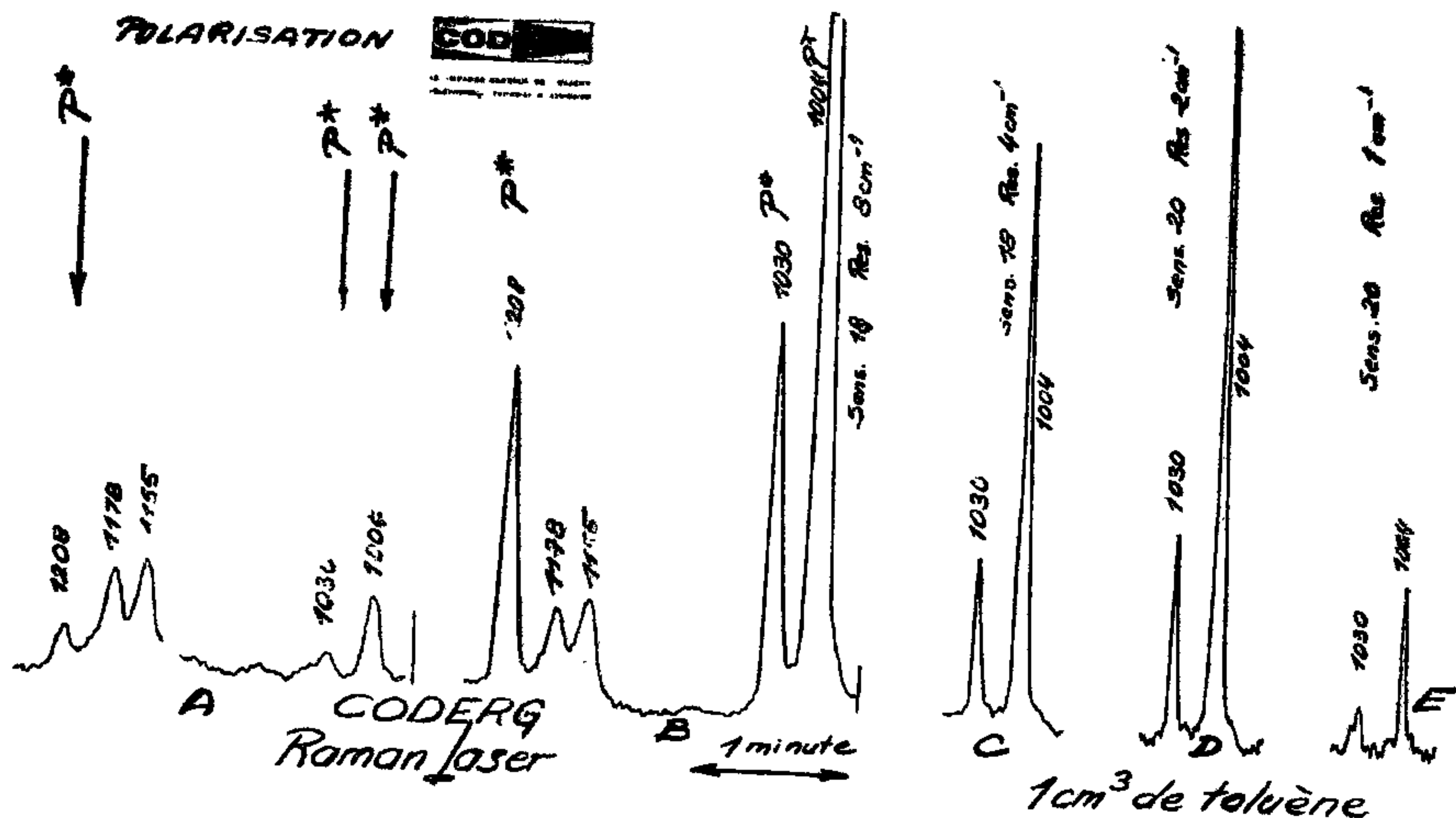


FIG. 1

while the frequencies observed in the infrared absorption are related to changes in the dipole moment.

The intensity of the Raman spectrum varies as the fourth power of the frequency. However, when a coloured substance is excited in the vicinity of an electronic absorption band, a considerable enhancement of the intensity is observed which is caused by the "resonance effect".

The measurement of the state of polarisation of the scattered light enables a classification of the different frequencies to be made: the rays that are polarised are due to symmetrical vibrations, and the rays that are unpolarised to antisymmetric or degenerate vibrations.

A RAMAN SPECTROMETER COMPLETELY DESIGNED FOR LASER EXCITATION

The properties of the laser that make them different from the classical Raman sources (Mercury, Helium, etc. lamps) are (1) their single frequency characteristics; (2) their high monochromaticity ($\Delta\mu \sim 0.004 \text{ cm}^{-1}$ for He:Ne lasers); (3) their parallelism (divergence less than $30'$ arc); (4) the high degree of polarisation of the exciting light; (5) the high instantaneous power attainable (for pulsed lasers); and (6) the high degree of coherence. Much of the success of the laser as a practical Raman source will depend on the kind of geometry used for the cell containing the sample, and on the light gathering efficiency of the optics employed.

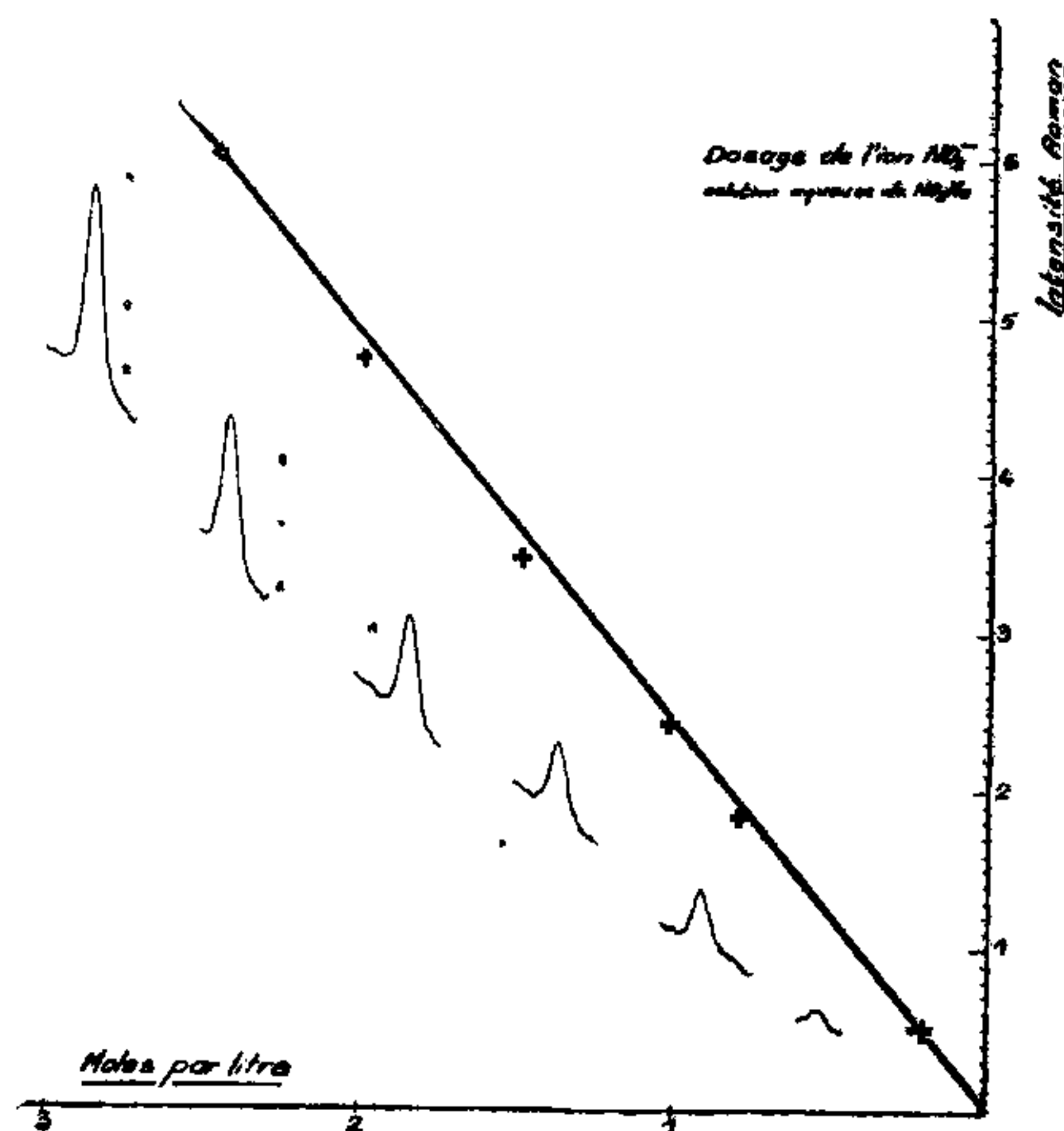


FIG. 2

To this day no commercial apparatus has fully taken advantage of all the qualities of the lasers for recording the Raman spectra. The CODERG (15, Impasse Barbier, 92-Clichy-France) have been trying to fill this lacuna, and with the help of the Comité "Instruments de mesure" and the "Délégation Générale à la Recherche Scientifique et Technique" they have succeeded in constructing a Laser Excitation

Raman Spectrometer that can stand comparison with any industrial infrared spectrophotometers, both with respect to the convenience of use and reliability, and with respect to the optical qualities. In this equipment the optical, mechanical and electronic elements have been specially designed to take into account the properties and the special geometry of the laser beam. The source is a He: Ne laser 50 mW 6328 Å (or Argon or ionized Krypton). The optics consist of a double monochromator—a grating followed by either a grating or a prism. The manufacturers claim that this equipment which is rapid, true, and automatised should

satisfy the most exacting researcher as well as the routine analyst.

The possibilities offered by this equipment are illustrated by the two figures reproduced here. Figure 1 presents a part of the toluene spectrum. The effect of polarisation of the lines 1208, 1030 and 1004, as well as the different resolutions on the last two lines could be seen. It is to be noted that the entire set of these results were obtained in about 10 minutes. Figure 2 represents a quantitative estimation of NO₃ ion, in an aqueous solution of NaNO₃ at different concentrations. In this case the entire set of results were obtained in 60 minutes.

SPECTROPHOTOMETRIC STUDIES OF MOLYBDENUM (VI) COMPLEX OF 3-PHENYLDAPHNETIN

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THOUGH the most common procedure for the colorimetric determination of molybdenum is based upon its colour formation with thiocyanate in presence of stannous chloride,¹ several phenolic compounds, e.g., catechol,² protocatechuic aldehyde,³ disodium-1, 2-dihydroxybenzene-3, 5-disulphonate,⁴ gallic acid⁵ have also been employed. Recently esculetin (6, 7-dihydroxycoumarin) and its derivatives have been used⁶ because they produce orange-coloured aqueous ethanol-soluble complexes with molybdenum. The present study deals with the complex of this metal with another dihydroxycoumarin, 3-phenyldaphnetin, i.e., 3-phenyl-7, 8-dihydroxycoumarin. Daphnetin derivatives have been used for a long time as mordant dyes, they can be expected to form stabler complexes useful for analytical work.

3-Phenyldaphnetin in ethanolic solution forms a yellow complex with molybdenum, which is soluble in 40% ethanol. This complex has molar composition of 1:1 and obeys Lambert-Beer's law, at 400 mμ, between the concentration limits of 1.7 to 5.7 ppm. of molybdenum in solution.

EXPERIMENTAL

3-Phenyldaphnetin was prepared by the method of Bargellini⁷ as improved by Krishnaswamy,⁸ and its standard ethanolic solution was used. Standard molybdenum solution was prepared using sodium molybdate (Analar BDH).

Beckman pH-meter model H2 was used for measurement of pH, which was adjusted with hydrochloric acid and sodium hydroxide.

Unicam spectrophotometer model SP 600 was used for spectrophotometric measurements.

Absorption spectrum of the complex.—The complex showed maximum absorption at 400–410 mμ between pH 1–7, thereby indicating the presence of only one complex. In this pH range of 1 to 7, the complex showed maximum absorption at pH 6, at 400–410 mμ. The subsequent studies were carried out at 400 mμ and at pH 6.

Minimum amount of the reagent for full colour development.—The study of the optical density of a series of solutions, containing the metal and the reagent in the ratio varying from 1:1 to 1:13, showed that the full colour development required a tenfold concentration of the reagent. During the subsequent studies, however, the molar ratio of the reagent to metal was maintained at 12.

Molar composition of the complex.—The molar composition of the complex was determined employing three different methods:

- Job's method of continuous variation⁹:**
This gives a composition of 1:1 as is indicated in Fig. 1.
- Mole-ratio method¹⁰:** The molar composition of the complex was also determined by the mole-ratio method of Harvey and Manning. The results indicate the composition to be 1:1 (Fig. 2).
- The composition was finally verified by Asmus method.¹¹** The straight line at $n=1$ shows the composition to be 1:1 (Fig. 3).