LETTERS TO THE EDITORS

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'Instantaneous' Presentation of Infra-Red Spectra on a Cathode Ray Screen

MANY of the recent advances in the application of infra-red spectroscopy to problems of molecular structure have been due to the greatly increased speed with which such spectra can be recorded. This makes it possible for the spectra of large numbers of compounds of known constitution to be compared, and so characteristic spectroscopic features of certain groupings can be established. While several spectrometers have been developed for recording an absorption spectrum (under moderately high resolving power) between $2\,\mu$ and $15\,\mu$ in a time of the order of half an hour, only one attempt[1] appears to have been made to obtain ultra high-speed presentation of spectra on a cathode ray screen. Yet the advantages of such a method are very great, the most obvious, perhaps, being the possibility which is thus opened up of studying rapidly changing spectra, such as those encountered in chemical kinetics, in changes of physical state and in emission from transitory flames.

The controlling factors in such a spectrometer are naturally the speed and sensitivity of the detector system. In the attempt referred to above, a bolometer with a time constant of $0\cdot089$ sec. was used together with a Moll microgalvanometer, the latter setting the limit of speed of response of the detector system at $0\cdot2$ sec. The method of presentation was such that 75 points in the infra-red spectrum were shown on the screen in a scan occupying one minute. Taking a slit width of 4 cm.$^{-1}$ as a reasonable value for the moderate resolving power required for the majority of applications, this means that one observation point per slit-width would give 300 cm.$^{-1}$ as the range of spectrum which could be kept under continuous observation. Although this can be accepted as a possible range for such an instrument, the speed of scanning is too slow for two reasons. The first is that spectra which change in a matter of seconds cannot be kept under satisfactory observation: the second is that a persistence time of one minute is not yet really practicable. It may be added that the description of this instrument indicated that all the difficulties had not been overcome and certainly no spectra were given from which one could judge the actual as against the calculated performance.

Below we reproduce two typical photographs of infra-red spectra presented as steady pictures on a cathode ray screen by an instrument which we have recently completed and full details of which will be given in a more appropriate journal. The upper photograph is of the emission spectrum of a Nernst filament in the region of $2\,\mu$. It will be observed that on top of the well-known 'Planck curve' are superimposed absorption bands at $1\cdot9\,\mu$ and $2\cdot76\,\mu$ due to water vapour
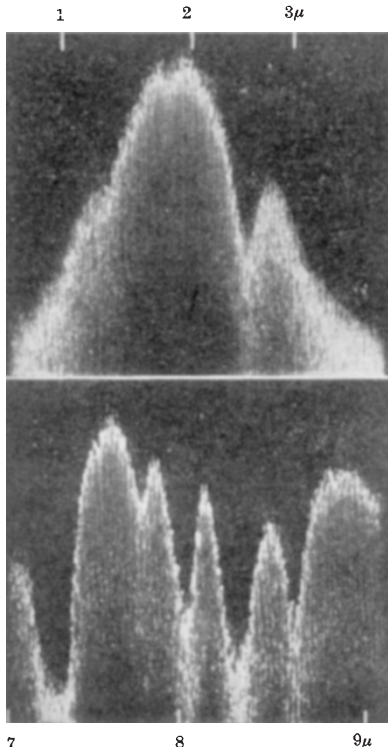
Above : EMISSION SPECTRUM OF A NERNST FILAMENT IN THE NEAR INFRA-RED $(1-4\,\mu)$.
Below : INFRA-RED ABSORPTION SPECTRUM OF LIQUID 2.2.4 TRIMETHYL PENTANE BETWEEN 7 AND $9\,\mu$ SHOWING BANDS AT $7\cdot3$, $7\cdot8$, $8\cdot0$, $8\cdot3$ AND $8\cdot6\,\mu$.

and carbon dioxide in the atmosphere. The lower photograph shows the absorption spectrum of 2.2.4 trimethylpentane between $7\,\mu$ $(1,430$ cm.$^{-1})$ and $9\,\mu$ $(1111$ cm.$^{-1})$. The time of the complete scan in each case is 14 seconds, and the persistence of the after image on the screen is so good that the spectrum is visible in a room with normal lighting. To give similar detail, the Baker and Robb apparatus would take approximately seven times as long to make the corresponding scan.

The detector used in this work was a thermistor bolometer developed in the Bell Telephone Laboratories for high-speed spectroscopic work ; it has a time constant of just less than $0\cdot01$ sec. Radiation from the infra-red source was interrupted at 15–20 cycles/sec. before passing through the absorption cell and spectrometer, and the output from the detector fed to an amplifier having a flat response to frequencies from 2 cycles/sec. to 40 cycles/sec. The instrument is thus rendered insensitive to draughts and slow temperature drifts, normally so troublesome in infra-red spectroscopy, but will follow accurately the rapid changes in radiation intensity which occur as a spectrum is scanned. Output from the amplifier is rectified and further amplified before being fed to the Y plates of a cathode ray tube. The tube used had a long-persistence screen, and is actually one of the type developed for 'P.P.I.' presentation in radar equipment.

The financial support for this research came from the Institute of Petroleum, as part of a programme of fundamental research on infra-red spectroscopy sponsored by that body. During part of the time this work was being done, one of us (E. F. D.) was in Admiralty employment, and we should like to express our thanks to the Admiralty for valuable assistance.

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Perturbations in the Band Spectrum of Beryllium Oxide

BeO has three well-known electronic states—all singlets. These are in order, the normal $^1\Sigma+$, then the two activated states $^1\Sigma^*+$ and $^1\Pi$. The $\Sigma^* - \Sigma$ bands[1,2] lie in the visible region, the $\Pi - \Sigma$ bands[3] in the infra-red. There are also bands in the ultra-violet[1,4], but the analyses of them are questionable.

In an investigation[5] of the infra-red $\Pi - \Sigma$ system, Westöö and I found six perturbations in the fine-structure of the vibrational levels 1, 2 and 3 in Π. Three of them are due to interactions from rotational levels in $v = 8$, 9, and 10 of the normal Σ-state.

Westöö and I[6] subjected the $\Sigma^* - \Sigma$ system to a rather detailed analysis, in which nine vibrational levels in the excited Σ^*-state were investigated up to high rotational quantum numbers in addition to seven vibrational levels in the ground Σ-state. Perturbations were found in the terms of Σ^*. Most of them can be explained by interactions with the Π-state. Thus rotational terms of the vibrational levels from $v = 11$ up to $v = 24$ in Π could be followed. L. Herzberg[3] analysed up to $v = 10$. It is of interest that her vibrational equation for Π proved to be valid even up to $v = 24$. Our analysis gives the following equation for the band-origins of the $\Sigma^* - \Sigma$ transition.

$$\nu_0{}^{(v,v)} = 19772\cdot52 + 1370\cdot817(v + \tfrac{1}{2}) - 7\cdot7455(v + \tfrac{1}{2})^2 - 0\cdot00027(v + \tfrac{1}{2})^3 - 1487\cdot323(v + \tfrac{1}{2}) + 11\cdot8297(v + \tfrac{1}{2})^2 - 0\cdot02235(v + \tfrac{1}{2})^3.$$

In an investigation[7] just finished, I have calculated the perturbing matrix elements for the $\Sigma\Pi$ and $\Pi\Sigma^*$ perturbations mentioned above from experimental data. For some perturbations extra lines appear. The most perturbed level is doubled. The intensity ratio for lines emitted from such a doublet is given theoretically by Dieke[8]. For three perturbations—at $J = 16$ in $v = 1,\Sigma^*$ and in $v = 12,\Pi$, at $J = 50$ in $v = 1,\Sigma^*$ and in $v = 13,\Pi$, and at $J = 81$ in $v = 1,\Sigma^*$ and in $v = 14,\Pi$—I determined the intensity ratio from intensity measurements, and then compared the results with the ratios calculated from the theoretical expression used in the displaced terms. The results were :

From intensity measurements	$14:1$	$6\cdot4:1$	$1\cdot65:1$
Theoretically	$15:1$	$5\cdot6:1$	$1\cdot7\ :1$

On careful investigation of the lower levels in Π, perturbations can be found in the R-, P- and Q-branches at $J = 56$–57 in $v = 1$, at $J = 48$–49 in $v = 2$, at $J = 40$–41 in $v = 3$ and at $J = 31$–32 in $v = 4$. Westöö and I[5] indicated the first three perturbations, but noted them only in the R- and P-branches. The perturbing levels evidently belong to rotational terms of consecutive vibrational levels in a hitherto unknown electronic state. As all three branches are perturbed, the perturbing levels must emanate from a $^1\Pi$- or a $^1\triangle$-state. It follows from the appearance of the perturbations that the perturbing state has a B-value smaller than that ($1\cdot35$ cm.$^{-1}$) of the known Π-state. Details of this will appear later.

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