Integration of Absorption Bands

DIFFERENTIATION of absorption bands has been dealt with fairly completely in recent years[1] and it is the purpose of this communication to consider some novel aspects of integration.

A convenient band shape for the present purpose is

$$A = \tfrac{1}{2}A_{\text{max.}}\,(1 + \cos x)$$

where x has the extreme values $-\pi$ and π, A is the absorbance and $x \propto \nu - \nu_0$ (ν is the frequency and ν_0 corresponds to the band maximum). On integration with addition of the appropriate constant,

$$\int A\,dx = \tfrac{1}{2}A_{\text{max.}}\,(x + \sin x + \pi) = F(x)$$

The result of plotting this expression is shown in Fig. 1*b*, together with the original band, Fig. 1*a*. Band-area is a valuable quantity, since it frequently affords a better measurement of band-intensity than peak height, which depends markedly on the resolution of the spectrometer used.

The application of a second stage of integration does not seem to have been considered previously. The resulting curve can vary considerably, as shown in Fig. 1*c* and *d*, depending on which point on $\int A\,dx$ is taken as zero. If the central point be taken, ($x = 0$), then:

$$\int F(x)\,dx = \tfrac{1}{2}A_{\text{max.}}\,(\tfrac{1}{2}x^2 - \cos x + 1)$$

and the resulting curve, Fig. 1*c*, bears some resemblance to the original absorption band; but in the more useful case where the commencement of $\int A\,dx$ is taken as zero,

$$\int F(x)\,dx = \tfrac{1}{2}A_{\text{max.}}\,(x^2/2 - \cos x + \pi x + \pi^2/2 - 1)$$

and there is no such similarity (Fig. 1*d*). It is easy to see that in *all* cases $\int A\,dx$ is equal to the difference between the initial and final slope of the doubly integrated absorption band.

In a practical case, using a spectrometer with amplifier giving a d.c. output which is applied to two conventional stages of electrical integration, the final capacitor charges (or discharges) at a constant rate, assuming a steady background, until the start of the absorption band is reached, then the double integration takes place and again the capacitor discharges (or charges) at a constant rate on completion of the band and reversion to a steady background. The difference between these two steady charging rates gives a measure of the band-area, $\int A\,dx$.

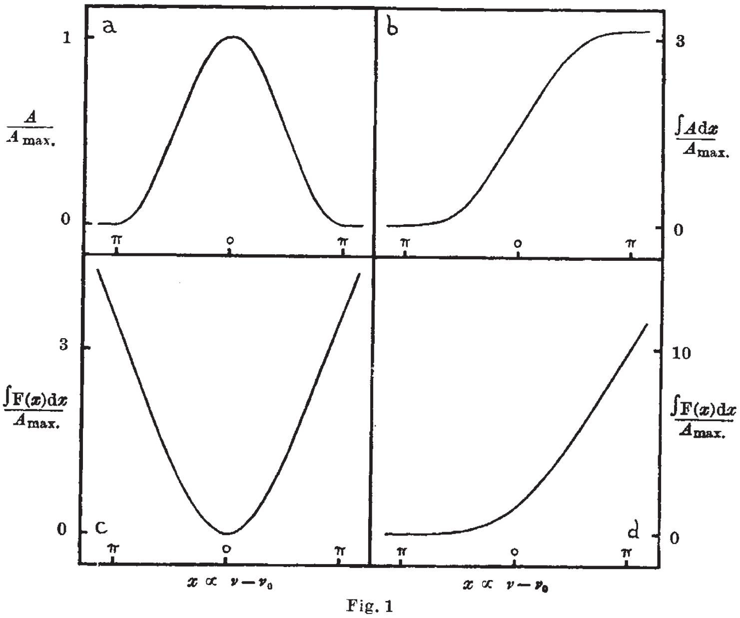

Fig. 1

The band twice integrated, and to a lesser degree that which has been integrated once, has an important advantage over the original in that the signal/noise ratio is greatly improved since, in general, noise in the output from a spectrometer amplifier occurs at a higher frequency than that of the signal. In fact, if the signal is represented by $a_1 \sin \omega_1 t$ and the noise by $a_2 \sin \omega_2 t$, after double integration the levels are $-(a_1/\omega_1^2) \sin \omega_1 t$ and $-(a_2/\omega_2^2) \sin \omega_2 t$, so that the signal/noise ratio has improved in the ratio ω_2^2/ω_1^2. This result may make the process of double integration of value in analytical work where it is necessary to measure a particular band with maximum accuracy.

A further important use for integration is to eliminate the effect of troublesome background absorption. If, for example, a small, sharp band is located on a steeply rising or falling background, this latter may be eliminated almost completely by differentiating once or twice, as may be necessary, and then reconstructing the band free from background by integrating once or twice, as required, with addition of one or two appropriate constants before or after integration.

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[1] Collier, G. L., and Singleton, F., *J. App. Chem.*, **6**, 495 (1956). French, C. S., Symposium on Instrumentation and Control, Berkeley, California, May 1957. Martin, A. E., *Nature*, **180**, 231 (1957); *Spectrochim. Acta* (in the press).

Determination of Radio-Propagation Elements due to an Artificial Earth Satellite

IN a previous communication[1] an easy method was developed for determining the refraction of a radio signal-path originating in a cosmical source and penetrating the ionosphere. It was stated there that the straight-line part of a ray-path, due to the un-ionized medium, will be turned about the centre of curvature of that layer, through which it penetrates, by an angle R defined by:

$$R = \frac{\sigma}{2}\left(\frac{fc}{f}\right)^2 \frac{\sin i_0}{\cos^3 i_0} \text{ in radians} \qquad (1)$$

or

$$R = \frac{90}{\pi}\left(\frac{fc}{f}\right)^2 \frac{\sin i_0}{\cos^3 i_0}\,\sigma \text{ in degrees}$$

The interpretation of the symbols used as well as the limits of validity of (1) are given in ref. 1 and also in Fig. 1.

An equally simple formula has been obtained for expressing the length of a radio path between a satellite and the recorder and for determining the virtual position of the radiating body relatively to the real one.

Under the same conditions as before, we can express the length of the radio path between a satellite S and the Earth E by: