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Abstract

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PHYSICS

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OBTAINING ABSORPTION SPECTRA WITH THE AID OF COLD LIGHT SOURCES

The usual arrangement of an apparatus for investigating absorption spectra is shown in Fig. 1. Here a is the light source, b is the cuvette with the substance under investigation, and v is the receiver of the incident radiation. If all the elements of the arrangement are at the same temperature, then the flux incident on the receiver from the source side is completely compensated by the flux emitted by the receiver itself, and its readings are equal to zero. If the temperature of the source is higher than the temperature of the receiver, then the flux of radiant energy in the positive direction (from the source to the receiver) exceeds the energy flux in the negative direction, and the receiver, being heated, gives positive deflections. If, however, a cooled body is placed at point a, $T_{\text{ist}} < T_{\text{pr}} = T_{\text{kyuv}}$, then the energy incident on the receiver will be less than the energy emitted by the receiver, as a result of which, being cooled, it will give negative deflections. The readings of the receiver will depend not only on the temperatures of the light source and the receiver, but also on the properties of the cuvette and, above all, on the absorption coefficient of the substance under investigation.

This circumstance, noted in (^{1}), is not difficult to use for obtaining absorption spectra with the aid of cold light sources.

Figure 2 shows a recording of the spectrum of nitrobenzene on an IKS-11 infrared spectrophotometer in the usual arrangement. The thickness of the cuvette, which was at room temperature, was 0.09 mm. The slit width was 1.9 mm. The zero line is drawn as a thin line. Line a gives the spectrum of a source of positive radiation (an electric furnace heated to +44°); line b is the spectrum of a source of negative radiation. A brass rod cooled with liquid air to −100° was chosen as the source of negative radiation. Curves v and g show the spectra of the first and second sources with nitrobenzene present in the cuvette. Figure 3 gives records for toluene, obtained under analogous conditions. From Figs. 2 and 3 it is seen that curves v and g possess good symmetry with respect to the

Fig. 1

Figure 1: Fig. 1

zero line; the positions of the absorption bands are completely identical. This result proves the possibility (and sometimes the advisability) of the practical use of sources of negative radiation flux. It should be borne in mind that the form of curves v and g depends not only on the absorption coefficient of the substance in the cuvette, but also on the temperature of the furnace and of the refrigerator, respectively. At other temperatures the symmetry of the curves would be disturbed.

Fig. 1

A check showed that for negative fluxes Bouguer' s law is obeyed. The values of the absorption coefficients calculated from the spectral records for positive and negative radiation fluxes are completely identical.

The results obtained show that, when working in the infrared region of the spectrum, it is essential to take into account the thermal emission of the receiver, as well as of the cell with the substance under investigation. In some cases

Fig. 2
Fig. 2

Fig. 3
Fig. 3

radiant energy will propagate from the receiver through the cell to the light source, and nevertheless, from the record obtained on the instrument, it is possible to calculate the absorption spectrum of the object under investigation.

The readings of the receiver in the most general case are proportional to the difference $E_{\text{inc}} - E_{\text{rec}}$, where E_{inc} is the spectral intensity of the radiation incident on the receiver, and E_{rec} is the spectral intensity of the radiation of the receiver itself. The quantity $E_{\text{inc}} = E_1 + E_2$ consists of two parts. The first part corresponds to the radiation of the light source, the second to the thermal emission of the substance contained in the cell.

Let us assume, for simplicity, that the light source is a blackbody with emissive power U_{src}. Some fraction (α) of the energy of the light source falls on the cell. The value of α is determined by the luminosity of the focusing system and by the dimensions of the light source, the cell, and the receiver. If the cell were absent, all the radiant energy would fall on the receiver. In the presence of the cell, the spectral intensity of the flux incident on the receiver will be $E_1 = (1 - R)\alpha U_{\text{src}} e^{-kl}$, where R is the reflection coefficient of the substance under investigation, l is the thickness of its layer, and k is the absorption coefficient.

The value of E_2 is not difficult to calculate on the basis of Kirchhoff' s law. The spectral intensity of the flux emitted by the cell is equal to $(1 - R)A_{\text{cell}}U_{\text{cell}} =$

$(1-R)(1-e^{-kl})U_{\text{cell}}$, where U_{cell} is Planck' s function at $T = T_{\text{cell}}$. Only part of this flux falls on the receiver: $E_2 = \beta(1-R)(1-e^{-kl})U_{\text{cell}}$. The value of the coefficient β is determined by the geometry of the system.

The emissive power of the receiver, which we take to be a blackbody, is equal to U_{rec}. Only part (γ) of all the emitted energy goes in the direction of the cell; moreover, the spectral intensity of the flux returning back is equal to $R\gamma U_{\text{rec}}$, and therefore $E_{\text{rec}} = (1-R)\gamma U_{\text{rec}}$.

The receiver readings are equal to

$$Y = b(E_{\text{inc}} - E_{\text{rec}}) =$$

$$= b[\alpha(1-R)e^{-kl}U_{\text{src}} + \beta(1-R)(1-e^{-kl})U_{\text{cell}} - \gamma(1-R)U_{\text{rec}}], \tag{1}$$

where b is a proportionality factor. If there is complete thermodynamic equilibrium in the system, then the temperatures of the light source, the cell, and the receiver are identical, and the energy fluxes between all elements of the arrangement are zero. In this case $Y = 0$. Setting in (1) $U_{\text{src}} = U_{\text{cell}} = U_{\text{rec}}$

and, taking into account that the latter equality is valid for any values of kl, we obtain

$$\alpha = \beta = \gamma. \tag{2}$$

Equality (2) was obtained by us from general thermodynamic considerations. It could also be obtained, moreover, using simple considerations of photometry and geometrical optics. Substituting (2) into (1), we finally obtain

$$Y = \alpha b(1-R)[U \quad e^{-kl} + (1-e^{-kl})U \quad - U \ ]. \tag{3}$$

Formula (3) contains many practically important special cases. It must be taken into account, for example, when measuring the temperature dependence of the absorption coefficient, as well as when measuring temperatures by the method of self-reversal of spectral lines. We are interested here in the most frequently encountered case $U \quad = U \quad$. In this case

$$Y = \alpha b(1-R)(U \quad - U \ )e^{-kl}. \tag{4}$$

Depending on the temperature of the light source and of the receiver, the values of Y may be either positive or negative. Independently of this, the transmittance of the system P is always positive. It is equal to the ratio Y/Y_0, where Y_0 is the receiver reading with an empty cuvette. The value Y_0 is equal to $\alpha b(U \quad - U \ )$, and, consequently,

$$P = (1 - R)e^{-kl}. \tag{5}$$

Formulas (4) and (5) are in good agreement with the experimental material presented and serve as the basis for the use of sources of negative radiation in measuring absorption coefficients.

All the effects described become significant only in the infrared region of the spectrum or at very high temperatures. In the visible region, the emission of the receiver is negligibly small, and possible negative fluxes cannot be registered.

It follows from (3) that measurement of the absorption coefficient k is possible even without any light source, by heating or cooling the substance of the cuvette. This method is based on measuring the thermal emission of the substance contained in the cuvette.

Formulas (3) and (4) are also applicable to the description of the negative opticoacoustic effect recently discovered by M. L. Veingerov, Ya. I. Gerlovin, and N. A. Pankratov ([2]).

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CITED LITERATURE

[1] B. I. Stepanov, *Optics and Spectroscopy*, **3**, issue 1, 3 (1957). [2] M. L. Veingerov, Ya. I. Gerlovin, N. A. Pankratov, *Optics and Spectroscopy*, **1**, 1023 (1956).

Note: Figure translations are in progress. See original paper for figures.

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