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The Effect of Index of Refraction on the Position, Shape, and Intensity of Infrared Bands in Reflection-Absorption Spectra*

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The effect of the index of refraction on the appearance of infrared bands is discussed for a newly developing method of obtaining the infrared spectrum of a thin layer on a metal surface. The term, reflection-absorption spectroscopy, is proposed as a designation for this technique. Band shapes and shifts are calculated for reflection-absorption spectra, using previously published values for the optical constants. Examples are shown which indicate that the variation of index of refraction for an extremely strong band causes considerable changes from the usual transmission spectrum, but that the reflection-absorption spectrum of a weak band is much like the transmission spectrum. The calculations done with published data on the 609 cm^{-1} band of Cu_2O are compared with experimental results obtained with an oxide layer formed on a copper surface.

INTRODUCTION

The main purpose of the paper is to investigate, theoretically and experimentally, the influence of the index of refraction† on a relatively new method of spectroscopy (*1-3*) which we shall call reflection-absorption spectroscopy (R-A spectroscopy). One of the motivations for the development of this technique is the desire to obtain an infrared absorption spectrum of a monolayer of adsorbed material on a metal surface. From such a spectrum, a great deal of information can be deduced about the constitution and geometric structure of the adsorbed molecules, giving insights into the basic nature of the adsorption process (*4*). In cases where infrared absorption bands of a gas are still detected after adsorption, shifts in the band positions can sometimes be interpreted in terms of the nature of the bonding to the surface. It, therefore, becomes very important with the R-A technique to investigate any band shifts which appear as a result of the technique itself. Information on the magnitude of band shifts (*5*) to be expected in reflection-absorption spectra is not generally available to the chemical spectroscopist, but is of critical importance to the interpretation of his spectra. This is also true of band splitting and the variation of absorption intensity with film thickness, both of which are discussed in this paper.

The R-A technique has been applied with promising results to adsorbed layers of gases (*6*) and of liquids (*7*) as well as to the study of oxide layers (*8*) and chemically produced protective films (*9*) on metals.

II. REFLECTION-ABSORPTION SPECTROSCOPY

The term, reflection-absorption spectroscopy, is suggested here to refer specifically to the method of obtaining the spectrum of a thin layer of material located on the highly reflecting surface of a metal. The

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† The convention used in the remainder of this paper refers to the complex index of refraction, $n = n - ik$, where n is called the index of refraction, and k is the extinction coefficient.

method is that of reflecting radiation from the sample-covered metal surface, using the appropriate angle of incidence and state of polarization. At first glance, one is tempted to refer to the method as a reflection technique and to refer to the resulting spectrum as a reflection spectrum. The results are very different, however, from the spectrum obtained by reflection from the surface of a bulk sample. In that case an increase in the extinction coefficient causes an increase in the reflectance and the very strong dependence on the index of refraction makes the bands quite asymmetrical. In the R-A spectrum, an increase in the extinction coefficient causes energy to be removed from the reflected radiation. The resulting spectrum looks like the usual transmission spectrum, with absorption bands appearing as bands of reduced energy.

At the second glance, it might appear that we are actually considering a usual transmission spectrum, with the radiation being transmitted through the sample layer, reflected at the metal surface, and transmitted again through the sample layer. When the sample layer is thin, compared to the wavelength of the incident radiation, this concept is inappropriate. The amplitude of the electric standing wave field in the thin layer becomes the important factor and the path length of a ray becomes meaningless. One might say that the problem is one of physical optics and not of geometrical optics. Reference (*1*) gives a more complete discussion of this point.

In transmission spectroscopy we usually associate an absorption band with the variation of extinction coefficient in a material. Actually there is a slight dependence of the position of the transmittance minimum on the index of refraction. We want to calculate the significance of such an effect on R-A spectra. Figure 1 shows the variation of the extinction coefficient, k, and the index of refraction, n, through the 609 cm^{-1} absorption band of Cu_2O, as measured by O'Keefe (*10*).

Using the method described in Ref. (*1*), we have used the data of O'Keefe to calculate the appearance of the reflection-absorption spectrum of the 609 cm^{-1} band of Cu_2O. Figure 2 shows the results of this calculation on films of six different thicknesses, giving the result for one reflection at an incident angle of 87° from a copper surface covered with a layer of Cu_2O.

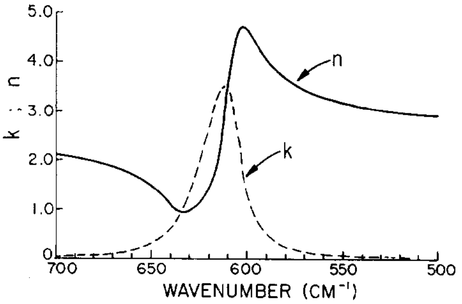

Fig. 1. The variation of n and k ($\tilde{n} = n - ik$) through the 609 cm^{-1} band of Cu_2O. Data from O'Keefe (*10*).

In all the cases treated in this paper we treat only that component of the radiation polarized parallel to the plane of incidence. The other polarization has been shown (*1*) to be insensitive to absorption bands in the thin layer. The plot of the extinction coefficient is given in curves *a* and *f* for comparison with the peaks in the reflection-absorp-

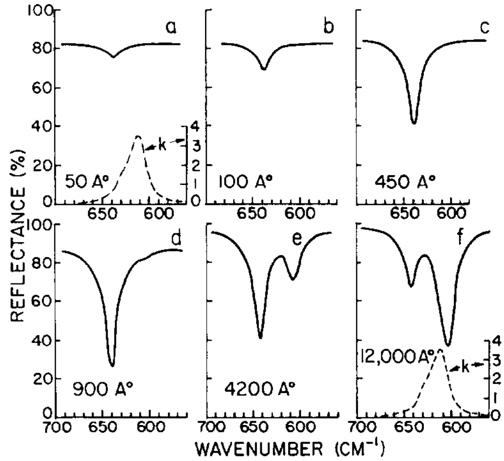

Fig. 2. Reflection-absorption spectrum calculated for the 609 cm^{-1} band of a Cu_2O film on a copper substrate. Calculation is done for angle of incidence of 87° using radiation polarized parallel to the plane of incidence. Each plot is calculated for a different thickness film. Optical constants used for the copper substrate are, $n = 25.8$; $k = 95.0$.

tion spectrum. The curves show several interesting features.

(1) For the thin layers (Fig. 2a, b, and c), the R-A spectrum shows only one band centered at 637 cm^{-1}. This is a shift of 28 cm^{-1} from the position of the peak in the extinction coefficient at 609 cm^{-1}. From Fig. 1 we see that the index of refraction has a minimum at 631 cm^{-1}. Calculations shown in Ref. (*1*) predict an increasing absorption for a decreasing value of n if other parameters are held constant. For these thin samples, the R-A band results primarily from the low value of n rather than the high value of k.

(2) For the thicker layers, (e.g., the 4200-Å layer, Fig. 2e) two bands appear in the R-A spectrum; one at 640 cm^{-1} and the other at 606 cm^{-1}. As before, the band at 640 cm^{-1} results from the minima in n but, with this thicker film, we see another band resulting primarily from the maximum value of k. In order to develop an intuitive understanding of the band shifts and splitting, we are discussing the effects of n and k on the R-A spectrum as if they were independent variables. We should remember that they are not independent; both depend upon the same absorption mechanism in the sample material. We could characterize the absorption process by either the variation of n or of k. The mathematical treatment, of course, take account of the simultaneous variation of both optical constants.

(3) The band appearing at 637 cm^{-1} for a thin oxide layer increases in intensity with increasing film thickness only to a certain point and then decreases for thicker films.

It should be kept in mind that results shown in Fig. 2 are for a very intense absorption band with an extinction coefficient of the order 50 times that of a typical, moderately strong band encountered in the infrared spectrum of short-chain hydrocarbon. Figure 3 shows the R-A spectrum calculated for the 1035 cm^{-1} band of liquid benzene using optical constant data from Gilby *et al.* (*11*). This band of benzene is used because it is a moderately strong band with a maximum extinction coefficient of 0.07. The plot for the thickest film includes a plot of the variation of k with wavenumber for comparison. For all the thicknesses shown in Fig. 3, the R-A band remains quite symmetrical and the position of the band coincides (to within 1 cm^{-1}) with the maximum value of k. Unlike the situation for the very intense band, we see essentially no band shift and no band doubling in the R-A spectrum. The consequence of this illustration is quite significant for the general usefulness of the R-A technique. It suggests that the R-A spectrum of typical moderately strong infrared bands should be directly comparable with the transmission spectrum. Since the bulk of the infrared reference literature is in the form of transmission spectra, this is a significant feature. Note also that the intensity of the R-A band does not increases monotonically with thickness, but goes through a maximum value.

III. EXPERIMENTAL CHECK OF PREDICTED EFFECTS

The calculations we have done for the reflection-absorption spectra of intense bands predict some shifts which should be easily

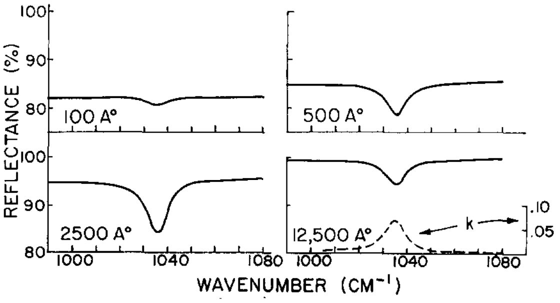

FIG. 3. Reflection-absorption spectra calculated for the 1035 cm^{-1} band of liquid benzene on copper. Calculation uses 87° angle of incidence and polarization parallel to the plane of incidence.

detectable by an experimental measurement. An experimental verification of the theoretical prediction would also give us confidence in other theoretical predictions which we use in the design of specific experiments and in the interpretation of experimental results.

As has been discussed, the effects of index of refraction on the R-A spectra are greater for stronger bands. The Cu_2O, 609 cm^{-1} band is an intense band for which we have optical constants data (*10*), and which is accessible to measurement with our equipment.

Measurements were made with a Beckman IR-9 spectrometer using the optical system described in Ref. (*2*). Figure 4 (taken from that reference) shows the auxiliary optical system and the two-mirror sample system used to obtain the reflection-absorption spectra. The copper films were deposited by thermal evaporation on glass sample plates 12 × 100 mm. The sample mirrors were located in the *f*/5 beam of the auxiliary optical system and were spaced 3 mm apart. This arrangement provided a spread of angles of incidence from about 84 to 90° with a maximum of three reflections for the extreme smaller angles of incidence and, more typically, one or two reflections for intermediate angles. Note that the requirements of this investigation are not for high sensitivity in detecting weak spectra but rather for a low number of reflections to study a very strong band. A polarizer was placed just before that monochromator entrance slit, polarizing both the sample beam and the reference beam. The polarizer is oriented to transmit radiation polarized parallel to the plane of incidence on the sample mirrors.

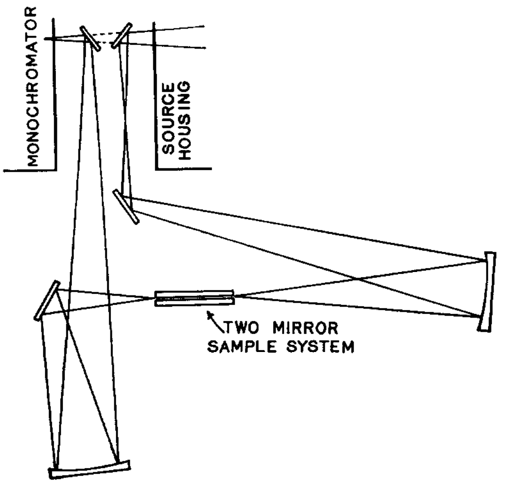

FIG. 4. Schematic view of optical system used to obtain reflection-absorption spectra.

The vacuum-deposited copper films were oxidized by being heated to a temperature of 145 ± 5°C in oxygen at a pressure of 175 ± 50 Torr. Using a multiple-beam interference technique, we measured the thickness of some films of copper, when they were freshly prepared and after they were completely oxidized. If we assume that the oxide layer on an incompletely oxidized copper film has the same density as that of the completely oxidized film, we can calculate the thickness of the oxide layer on a copper film from two thickness measurements, made before and after the oxidation process.

Figure 5 shows the infrared transmission spectrum of copper oxide. The sample was made by oxidizing a 500-Å film of copper for 1000 min. The oxide was scraped off the glass substrate, ground with KBr, and pressed in a die to form a sample pellet. The

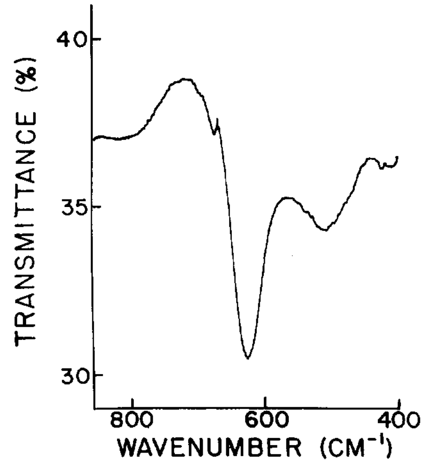

FIG. 5. Infrared transmittance of copper oxide in a KBr pellet. The oxide was formed by completely oxidizing an evaporated film of copper. The film was oxidized in the same system at the same temperature as those used for the reflection-absorption spectra shown in Fig. 6.

band at 623 cm^{-1} is located in the same place as is the large band we obtain from a KBr pellet spectrum of Cu$_2$O (cuprous oxide, reagent, General Chemical Co.). (In Fig. 5, the band appears to be located at 625 cm^{-1} due to a pen-chart registration error.) This strong absorption band has been reported by Pastrniak (*12*) to be at 610 cm^{-1}, by Terada (*13*) to be at 617 cm^{-1}, by O'Keefe (*10*) to be at 609 cm^{-1} and by Poling (*8*) to be at 620 cm^{-1}. The band at 500 cm^{-1} agrees with the strong band we obtained in the spectrum of CuO (CuO, 99.999%, Electronic Space Products, Inc.) in a KBr sample pellet.

One factor, which could complicate the results of these measurements, should be discussed. Wieder and Czanderna (*14*) report that Cu$_2$O is not formed in thin films (200–2400Å) by heating copper in an oxygen atmosphere. They report an oxide phase with a composition indicated by the formula, CuO$_{.67}$, which is stable at an oxygen pressure of 100 Torr for temperatures between 100 and 200°C. Similar results are reported by Hapase (*15*). According to Wieder and Czanderna, CuO$_{.67}$ and Cu$_2$O have the same X-ray diffraction and electron-diffraction lines. They were able to distinguish between CuO$_{.67}$ and Cu$_2$O by optical transmission (6000 Å region), density measurements, and oxygen uptake measurements with a microbalance. They conclude that CuO$_{.67}$ is a gross, defect structure of Cu$_2$O with one copper atom missing per unit cell, and that, although CuO is the only thermodynamically stable oxide at 100 Torr, CuO$_{.67}$ is more readily formed. Our density measurements of the oxide film agree with Wieder and Czanderna's data for CuO$_{.67}$. The infrared absorption band in the transmission spectrum at 623 cm^{-1} which we measure for these samples (see Fig. 5) coincides with that for commercially prepared Cu$_2$O. We will assume that the infrared spectra of Cu$_2$O and CuO$_{.67}$ are the same and compare the measurements on our films (which may be CuO$_{.67}$) with calculations based on the data of O'Keefe (*10*) obtained from reflection measurements on single-crystal copper oxide (which is assumed to be Cu$_2$O).

The measured R-A spectra of the oxide layer on a copper film are shown in Fig. 6 for oxide layers of four different thicknesses. All four show a strong band with center at 655 ± 4 cm^{-1}. For thicker oxide films, resulting from longer oxidation time, a band develops at about 550 cm^{-1}. This band can be seen in Fig. 6d as a shoulder on the main band. We interpret the 655 cm^{-1} band to be the Cu$_2$O (or CuO$_{.67}$) band, observed at 623 cm^{-1} in the transmission spectrum and the 550 cm^{-1} band to be the CuO band, observed at 500 cm^{-1} in the transmission spectrum. This represents a shift of +32 cm^{-1} for the Cu$_2$O (or CuO$_{.67}$) band, for

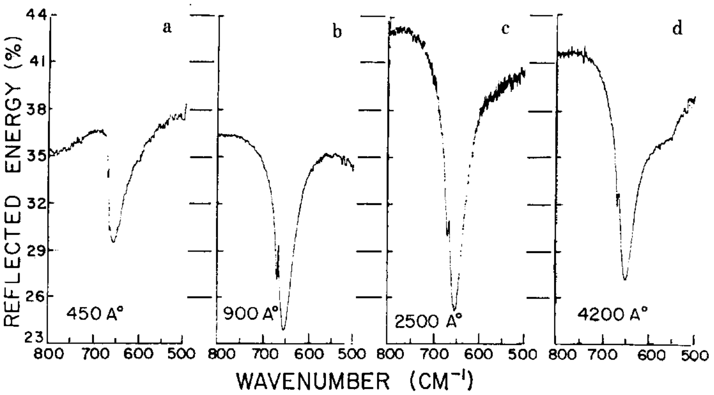

FIG. 6. Experimental reflection-absorption spectra of a copper oxide film on a copper substrate for different oxide thicknesses. The thicknesses of the films are: (a) 450 ± 150 Å, (b) 900 ± 150 Å, (c) 2500 ± 300 Å, and (d) 4200 ± 300 Å. The spectra are a result of radiation having angles of incidence from 84 to 90° and a number of reflections which depend on the angle of incidence.

which we have done calculations, and a shift of +50 cm^{-1} for the CuO band, for which we have no optical constants data. A trace of the 667 cm^{-1} band of CO_2 can be seen on all curves. This results from the residual CO_2 in the unbalanced arms of the sample system, even after vigorous flushing with dry nitrogen. The 2350 cm^{-1} band of CO_2 was monitored after each scan to determine the amount of uncompensated CO_2 and to insure that it did not interfere with the oxide band measurements.

The shifts agree reasonably well with those reported by Poling (*9*) (+20 cm^{-1} and +50 cm^{-1}). Poling's measurements were made at an angle of incidence of 73° and compared with prediction from the approximate expressions of Francis and Ellison (*3*). These equations involve approximations which make them invalid for high angles of incidence (typically for angles greater than about 80°). The method described in Ref. (*2*) uses angles of incidence approaching 90°; therefore, comparisons are needed with the exact calculations described in Ref. (*1*).

IV. Discussion

The cause of the variation in the reported locations (*8, 10, 12, 13*) of the absorption band at about 623 cm^{-1} is not obvious. It could result from physical or chemical difference in sample material or from errors in spectrometer calibration. It would seem that the most effective way to compare experimental results with theoretical prediction is to compare our measured band shifts with the calculated shifts, rather than comparing band positions. We have measured a shift of +32 cm^{-1} between the KBr pellet, transmission spectrum and the experimental R-A spectrum of copper oxide. Note that the copper oxide for both of these measurements was prepared in the same way, by heating the evaporated copper film in oxygen, and would be expected to be the same oxide material. This measured shift of 32 cm^{-1} is to be compared with the calculated shift of 28 cm^{-1} between the peak k value and the R-A spectrum. The agreement is reasonably good. To refine the comparison we might investigate the small shift which can occur in transmission spectra. In general for very strong bands the transmittance minimum is shifted to slightly lower wavenumbers from the peak k value. For example, using O'Keefe's data and exact expressions for transmittance (*16*) which take account of both n and k, we have calculated the shift expected for a thin film of copper oxide on a KBr slate. For films in the thickness range of a few hundred Angstroms the transmittance minimum is shifted -4 cm^{-1} from the peak k value. Taking account of such effects should even improve the agreement between the calculated and experimentally determined shift between the transmission spectrum and the R-A spectrum.

The band doubling predicted in Fig. 2 is not observed experimentally. The R-A peaks calculated from O'Keefe's data are much sharper than the peaks measured in these experiments. The broadening of the experimental peak shown in Fig. 6d is enough to wash out the calculated doubling of the peak, shown in Fig. 2e. Note that the appearance of the 500 cm^{-1} band in Fig. 6d is not evidence of this predicted doubling but is attributed to CuO which appears in thick oxide layers. Under the conditions of this experiment, it appears that $CuO_{.67}$ (or Cu_2O) is first formed and goes to CuO for long oxidation times. The broadening of the experimental bands may result from the small crystal size of the oxide layer grown on a thermally evaporated metal film. The optical constant data used for the calculations were derived from measurements made on single-crystal Cu_2O. It would be interesting to examine the absorption band in an oxide layer grown on a single crystal copper substrate.

The curves of Fig. 3 clearly illustrate the prediction that the band intensity does not monotonically increase with film thickness. (This does not appear to be the prediction of Fig. 2 where the band appearance is complicated by the band splitting.) The sequence of curves shown in Fig. 6 exhibits this dependence of band intensity on thickness; the intensity going through a maximum between the thickness of the film shown in curves 6b and d. We should keep in mind that the calculation treats one reflection at an angle of incidence of 87°, based on the single-crystal optical constants. The experimental measurements are the results of a spread in angles of incidence with a variable number of reflection on polycrystalline films.

V. SUMMARY

The prediction of a shift in position of a very strong band, as seen in the R-A spectrum, and of the relationship between the band intensity and film thickness are confirmed by experimental measurements. Calculations show that the position of moderately strong bands in the R-A spectrum should agree with their position in a transmission spectrum.

REFERENCES

1. GREENLER, ROBERT G., *J. Chem. Phys.* **44,** 310 (1966).
2. GREENLER, ROBERT G., *J. Chem. Phys.* **50,** 1963 (1969).
3. FRANCIS, S. A., AND ELLISON, A. H., *J. Opt. Soc. Amer.* **49,** 131 (1959).
4. LITTLE, L. H., "Infrared Spectra of Adsorbed Species," Academic Press, Inc., New York, 1966; HAIR, M. L., "Infrared Spectroscopy in Surface Chemistry," Marcel Dekker, Inc., New York, 1967.
5. Suëtaka has calculated the appearance of two infrared bands as seen by this technique and shows band shifts and band shapes for three angles of incidence. SUËTAKA, W., *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A* **18,** *Suppl.,* 129 (1966).
6. BRADSHAW, A. M., PRITCHARD, J., AND SIMS, M. L., *Chem. Commun.* 1519 (1968).
7. SUËTAKA, W., *Bull. Chem. Soc. Jap.* **38,** 148 (1965); *Bull. Chem. Soc. Jap.* **40,** 2077 (1967).
8. POLING, G. W., *J. Electrochem. Soc.* **116,** 958 (1969).
   HANNAH, R. W., *Appl. Spectrosc.* **17,** 23 (1963).
   BABUSHKIN, A. A., *Russ. J. Phys. Chem.* **38,** 1004 (1964).
9. POLING, G. W., *J. Electrochem. Soc.* **114,** 1209 (1967).
10. O'KEEFE, MICHAEL, *J. Chem. Phys.* **39,** 1789 (1963).
11. GILBY, A. C., BURR, J., KRUGES, W., AND CRAWFORD, B., JR., *J. Phys. Chem.* **70,** 1525 (1966).
12. PASTRNIAK, I., *Opt. Spectrosc. (USSR)* **6,** 64 (1959).
13. TERADA, M., *Bull. Chem. Soc. Japan* **37,** 766 (1964).
14. WIEDER, H., AND CZANDERNA, A. W., *J. Phys. Chem.* **66,** 816 (1962); *J. Appl. Phys.* **37,** 184 (1966).
15. HAPASE, M. G., *Surface Sci.* **9,** 87 (1968).
16. HEAVENS, O. S., "Optical Properties of Thin Films," p. 76. Academic Press, Inc., New York, (1955).