

- 1943, 541. Farmer, E. H., and Sutton, D. A., *Ibid.*, **1944**, 242. Bollond, J. L., and Koch, H. P., *Ibid.*, **1945**, 445. Atherton, D., and Hilditch, T. P., *Ibid.*, **1944**, 105.
- (2) Patton, S., Kenney, M., and Kurtz, G. W., *J. Am. Oil Chemists' Soc.*, **28**, 391 (1951).
- (3) Patton, S., and Kurtz, G. W., *J. Dairy Sci.*, **34**, 669 (1951).
- (4) Bernheim, F., Bernheim, M. L. C., and Wilbur, K. M., *J. Biol. Chem.*, **174**, 257 (1947).
- (5) Prill, E. A., *Oil and Soap*, **19**, 107 (1942).
- (6) Myddleton, W. W., *J. Inst. Petroleum*, **37**, 45 (1951).
- (7) Rothenbach, E., *Wochenschrift für Brauerei*, **56**, 273 (1939).

THE INFRARED C—H FREQUENCIES AT 13.8 μ AND THEIR SIGNIFICANCE*

By F. C. NACHOD, E. T. HINKEL, JR., and M. PRIZNAR

Sterling-Winthrop Research Institute, Rensselaer, N. Y.

AN ABSORPTION BAND in the 13.8 μ region of hydrocarbons and its unusual behavior in a series of compounds have been the subject of theory and speculation for some time. A doublet at about 13.85 μ was first pointed out by Thompson and Torkington (1) who ascribed it to a deformation vibration in the CH₂ group of long straight-chain molecules. They also pointed out that liquid paraffins do not exhibit the doublet which appears in the spectrum of polyethylene. Molecular weight changes from 500 to 13,000 of the polymer did not alter the shape of the doublet significantly.

Elliot, Ambrose, and Temple (2) found that using polarized infrared radiation caused the disappearance of the doublet and the formation of a single broad band. The disappearing component was ascribed to the rocking vibration mode of the CH₂ groups across the chain. Simanouti (3) considered this perturbation (at 728 $\bar{\nu}$) as perpendicular to the chain axis.

* Received for publication, Aug. 9, 1954.

TABLE I—CH₂ BAND APPEARANCE

Doublet (13.72 μ and 13.92 μ)		Single Band (13.92 μ)	Inflection Point (13.79 μ)
Adurco Wax	Palm Wax	Bayberry Wax	Raphia Wax
Barnsdall Amber	Plio Wax	Butyl Stearate	White Ceresine Wax
Beeswax	Polyethylene	Glyceryl Monostearate	
Carnauba Wax	Spermatine Wax	Japan Wax	
Candelilla	Spermaceti	Lanolin	
Crown 1035	Stearic Acid	Shellac	
I G Wax B unbleached	Stearyl Alcohol		
I G Wax E	Sugar Cane		
I G Wax OP	Utah Wax		
I G Wax S	Petrolatum		
I G Wax Z	Vegetable Wax		
Ozokerite			

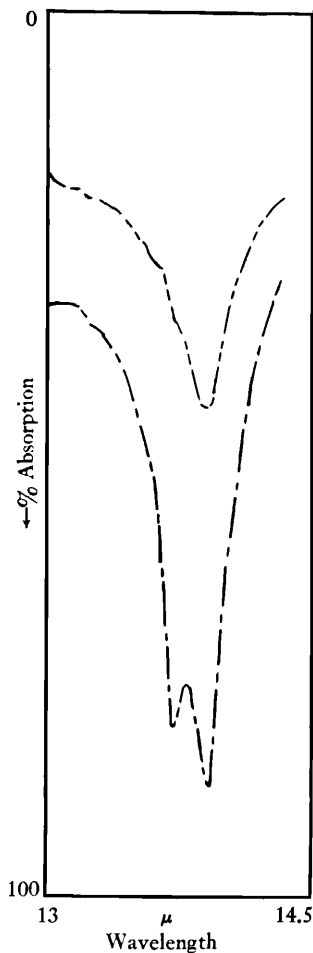


Figure 1.—Absorption spectrum of petrolatum: top curve, molten, 75°; bottom curve, solid 23°.

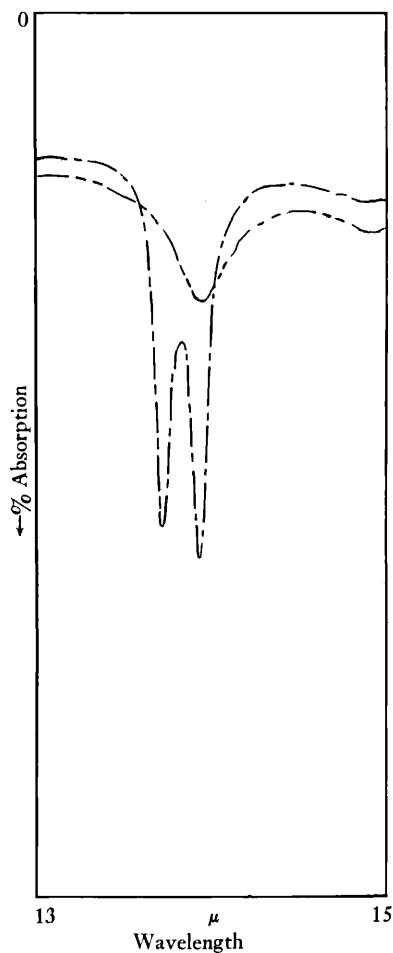


Figure 2.—Absorption spectrum of I G Wax Z: ——— solid, room temp.; - - - - molten, 120°.

Others have studied *n*-paraffins such as *n*-nonane, *n*-decane, and *n*-tetradecane in crystalline state (4) and observed the doublet, and Sutherland (5) correlated it with the transition point of the substance. The doublet persists until the transition point is reached but is a singlet in the liquid state.

Our own observations have borne out this observation. Figure 1 shows the 13–15 μ region of the infrared absorption spectrum of petrolatum, which essentially consists of *n*-hydrocarbons. Upon melting, the doublet disappears but can be recovered if the sample is placed shortly on a piece of

dry ice in order to resolidify it. The same behavior at a higher transition temperature can be demonstrated for the case of I G wax Z, shown in Fig. 2.

That the doublet disappears not only on melting but also upon dissolving is shown in Fig. 3 for Utah wax where the solution in iso-octane shows but the single band.

The most satisfying explanation of what he terms "infrared dichroism" has just been advanced by Krimm (6) who pointed out that the two components arise from in-phase/out-of-phase rocking of CH_2 groups on adjacent chains.

The importance of infrared measurements and observation in the cosmetic industry has been pointed out repeatedly (7, 8). We have studied a number of natural and synthetic products (Table 1) particularly with reference to the doublet CH_2 -rocking effect. From the above remarks we believe that this phenomenon permits a statement as to the nature, i.e., linearity of the hydrocarbon portion of the solid material under observation and constitutes a useful qualitative analytical parameter.

It should be pointed out that glyceryl monostearate, and both Bayberry and Japan wax, which are mainly glycerides, do not show the doublet. A possible explanation could be that the glyceryl portion of the molecules prevents them from packing close enough for the CH_2 in adjacent chains to show any in-phase/out-of-phase rocking.



Figure 3.—Absorption spectrum of Utah wax: — iso-octane, solvent; --- Utah Wax in iso-octane; ——— Utah Wax, solid, room temp.; - - - - Utah Wax, molten, 120°.

BIBLIOGRAPHY

- (1) Thompson, H. W., and Torkington, P., *Proc. Roy. Soc.*, **A184**, 3 (1945).
- (2) Elliot, E. J., Ambrose, E. J., and Temple, R. B., *J. Chem. Phys.*, **16**, 877 (1948).
- (3) Simanouti, T., *Ibid.*, **17**, 734 (1949).

- (4) Brown, J. K., Sheppard, N., and Simpson, D. M., *Discussions Faraday Soc.*, **9**, 261 (1950).
- (5) Sutherland, G. B. B. M., *Ibid.*, **9**, 274 (1950).
- (6) Krimm, S., *J. Chem. Phys.*, **22**, 567 (1954).
- (7) Bernstein, R. B., *J. Soc. COSMETIC CHEM.*, **3**, 265 (1952).
- (8) Hausdorff, H. H., *Ibid.*, **4**, 251 (1953).

RECENT PROGRESS IN THE CHEMISTRY OF DI-SULFIDES*

By NORMAN A. ROSENTHAL and GERALD OSTER†

*Institute for Polymer Research, Polytechnic Institute of Brooklyn,
Brooklyn, N. Y.*

I. INTRODUCTION

THE WIDESPREAD occurrence in nature of compounds containing sulfhydryl and disulfide groups forces one to accept these substances as being essential in the chemistry of living processes. The important role of naturally occurring sulfhydryl compounds such as glutathione and cysteine in the oxidative processes taking place in living cells was emphasized by Hopkins and his co-workers at Cambridge University many years ago. The role of sulfur in intermediate metabolism and its implications to medicine have been ably summarized in the recent book of duVigneaud (1). It has even been suggested that sulfur-containing compounds may play a critical role in photosynthesis (2) and in vision (3).

The large body of research on the chemistry of proteins carried out over the past half century has established that the disulfide linkage is an important structural element in proteins. The liberation of sulfhydryl groups when proteins are denatured may indicate that disulfide groups are holding the protein structure together and that they are ruptured on denaturation (4). The detailed studies of Sanger (5) have shown that the polypeptide chains of insulin are held together by disulfide bonds. Keratin is particularly rich in disulfide bonds and, for the case of wool and hair, cystine is found in greater abundance than any other single amino acid. Most of the chemical treatment of wool and hair is concerned with the rupture and reformation of the disulfide bond. It is obvious, therefore, that any rationalization of the process employed, for example, in permanent hair waving must require a complete understanding of the chemistry of the disulfide linkage.

* Presented at the May 14, 1954, Meeting, New York City.

† Taken in part from the thesis submitted by Norman A. Rosenthal in partial fulfillment for the requirements for the degree of Doctor of Philosophy.