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STUDIES IN THE INFRARED—I

[l (–) allo-hydroxyproline and rutile]

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ABSTRACT

The infrared absorption spectra of *l* (–) allo-hydroxy proline and rutile have been investigated using a Perkin Elmer Model 112 single beam recording spectrometer. The spectrum of the former consists of 13 bands in the region 1 to 13 μ, and it has been found possible to explain these with the help of the known approximate frequencies of the structural groups and the chemical constitution of *l* (–) allo-hydroxyproline. On the other hand the absorption spectrum of rutile reveals a rather broad absorption from 1,700 cm.$^{-1}$ to 1,975 cm.$^{-1}$ and also two bands at 1,548 and 1,524 cm.$^{-1}$ These three bands and also the four bands observed by Randall *et al.* for white rouge between 8 to 15 μ are found to coincide with the approximate calculated frequencies of the infrared active combinations and harmonics of the frequencies of rutile.

1. INTRODUCTION

The growing importance of infrared spectroscopy for the study of the fundamental problems connected with the vibration spectra of substances, as a tool for a qualitative as well as a quantitative analysis of mixtures and also for the establishment of molecular structures in the field of organic chemistry is well known. But experimental difficulties have always stood in the way of exact studies and rapid progress in the infrared has not been possible till recently for lack of sources of adequate strength, suitable transparent prism materials, rapid and sensitive receivers, etc. Most of these are in the process of being eliminated and with a modern commercial prism spectrometer it is possible to obtain a resolution which could be had formerly only with gratings. Recently a Perkin Elmer model 112 single beam automatic recording spectrometer with a rocksalt prism became available for such studies at this laboratory and it is proposed to give here the preliminary results in two representative cases of study since a much desirable extension of the work is not possible for some time due to unavoidable reasons.

2. EXPERIMENTAL DETAILS

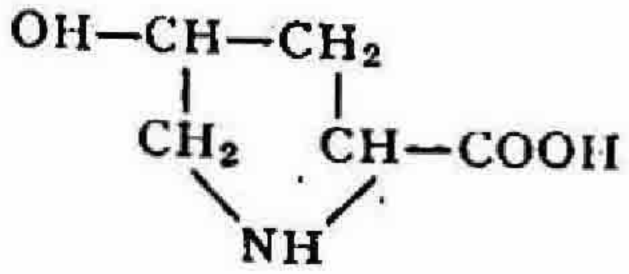
The spectra were studied with a single beam double pass infrared spectrometer. Two different samples of *l* (–) allo-hydroxyproline, one of which was isolated by Greenstein, and known to be quite pure were kindly placed at our disposal for the present study by Prof. K. V. Giri to whom our thanks are due.

The *l*(-) allo-hydroxyproline which was in the form of crystalline powder was mulled in paraffin oil and the absorption due to the oil was allowed for and the true percentage transmission curve was drawn through a point by point division of the records obtained with the pure paraffin oil and the mulled sample held in a demountable liquid cell. The presence of the CH frequencies in paraffin at 3·43, 3·51, 6·85 and 7·25 rendered it difficult to study very accurately that of the sample at these points.

The infrared absorption spectrum of rutile was studied using three thin plates cut from a single boule of optical quality manufactured by Linde Air Products Co., Inc., U.S.A. The plates were of thicknesses 0·57, 0·3 and 0·26 mm. respectively. They were cut in such a way that the surfaces were nearly parallel to the optic axis. The percentage absorption curve was obtained using the same procedure as in the case of the mulled sample. Even with the thinnest specimen the absorption beyond $7\,\mu$ was so large that measurements could not be pushed beyond that.

3. RESULTS AND DISCUSSION

The infrared absorption spectra of both samples of hydroxyproline were essentially identical. The structural formula of the hydroxyproline is known to be



(Takeo Kaneko, 1940). The spectrum consists of a broad band extending from 2 μ to nearly 4·5 μ with the maximum at 2·48 μ and a series of comparatively weak absorption bands with maxima at 1548 (6·46), 1475 (6·78), 1282 (7·8), 1216 (8·22), 1111 (9·01), 1059 (9·44), 1016 (9·84), 990 (10·1), 931 (10·75), 874 (11·44), 836 (11·96) and 824 cm.$^{-1}$ (12·13 μ) (Fig. 1). Of these, the first, a broad band, is characteristic of the spectra of all amino-acids and in this particular case the unusually large width is probably due to the overlapping of the OH as well as CH stretching vibrations. In the double bond region one observes two bands (6·46 and 6·78 μ) of moderate intensity. In the same region *l*-proline (Randall *et al.*, 1952) exhibits also two bands (6·17 and 6·40 μ), the former being attributed to the carboxylate ion. However, the absorption peaks in hydroxyproline are shifted considerably to the long wavelength side and it seems improbable that this should be due to the carboxylate ion as in *l*-proline. The absorption bands arising from the NH bending vibrations are to be expected in the double bond region. Though ordinarily the secondary amines do not show a band of any strength, it seems fairly reasonable to suppose that in this case the 6·46 and 6·78 μ bands may be interpreted as arising from the NH bending vibrations.

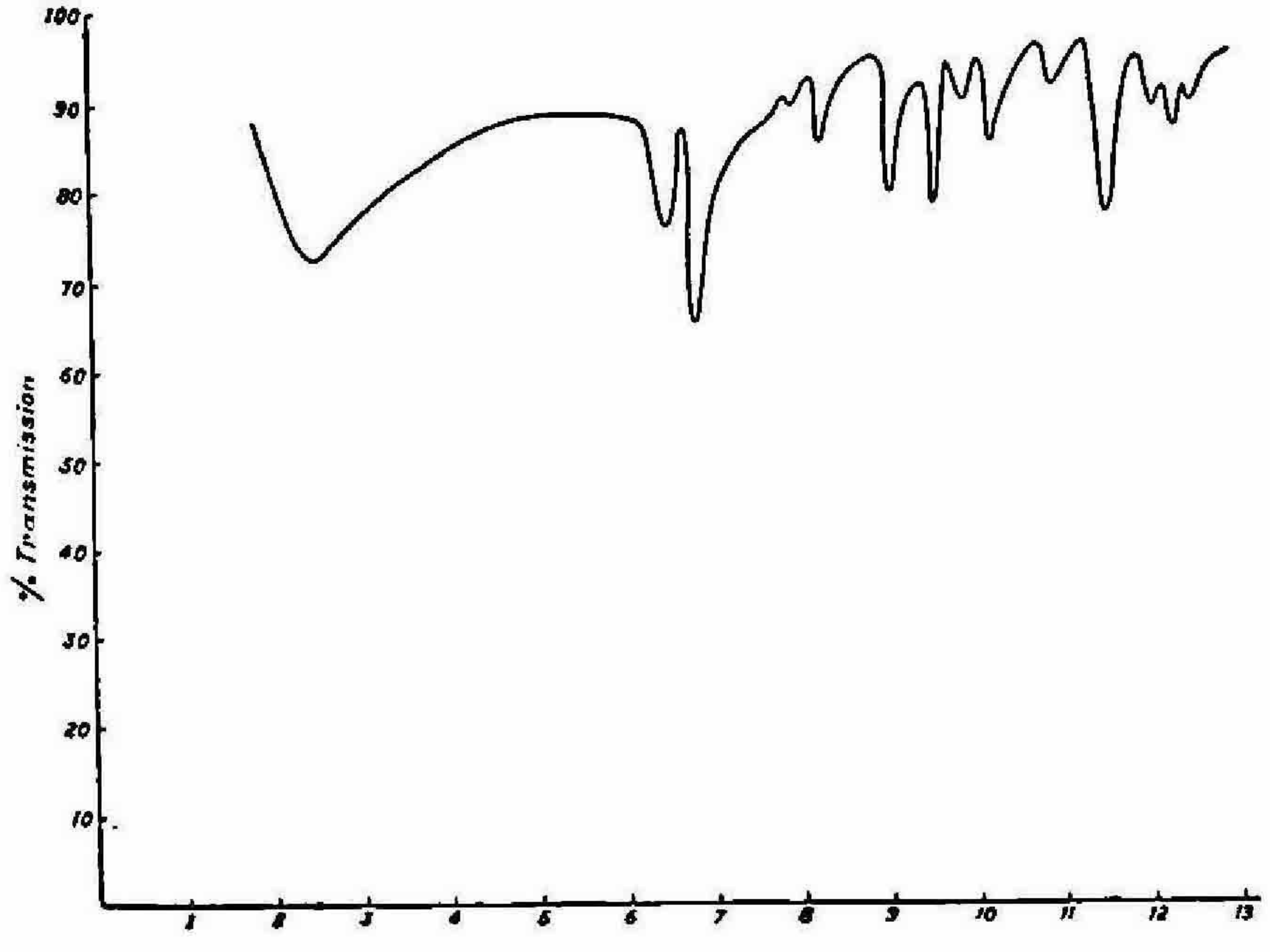


FIG. 1. Infrared Spectrum of *e* (—) allo-hydroxyproline

The two bands at 7·8 and 8·22 μ almost coincide with those observed in *l*-proline hydrochloride (Randall *et al.*, *loc. cit.*) at 7·81 and 8·21 μ and are associated with OH bending vibrations.

On the longer wavelength side of 8 μ, the specific bond frequencies which essentially arise from single bonds for such groups as ethyl, propyl, aldehyde, ketone, etc., produce relatively weak bands which are quite sensitive to the manner in which these groups are attached to the rest of the molecule. Consequently, while it is reasonable to presume that the bands 11·44, 11·96 and 12·13 μ are due to some type of bending oscillations of NH and CH and the remaining five 9·01, 9·44, 9·84, 10·1 and 10·75 due to the single bond stretching vibrations, it is necessary to make a theoretical study of the possible vibrations taking the molecule as a whole and taking into account the mutual interaction of the different groups before definite conclusions can be arrived at.

A comparative study of the absorption curves of rutile (TiO_2) for the three thicknesses specified above reveals a rather broad absorption from 1,700 cm.$^{-1}$ to 1,975 cm.$^{-1}$ with maximum at 1,852 (5·4) and also two bands at 1,548 (6·46) and 1,524 cm.$^{-1}$ (6·56 μ). (Fig. 2). Since carrying out this investigation with single crystals, it has come to our notice that in the case of crystal plates polished with white rouge (titanium dioxide) certain absorptions are noticed (Randall *et al.*, *loc. cit.*, page 92). These comprise of a strong broad absorption from 8·3 to 9·5 μ, a medium strong line at 12 μ and two weaker lines at 12·82 and 14·38 μ.

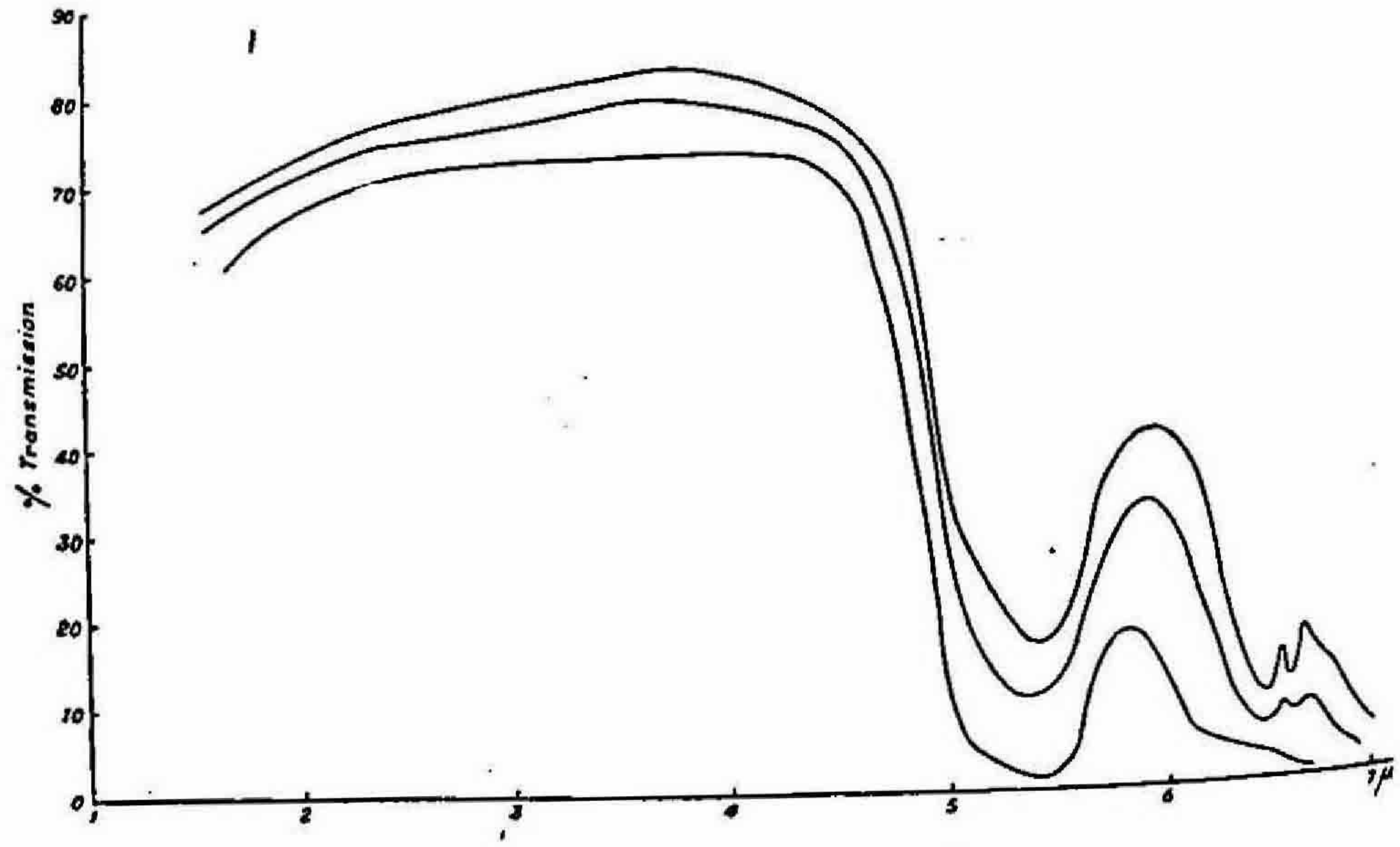


FIG. 2. Infrared Spectrum of Rutile

For an interpretation of the observed infrared absorption one may apply the group theoretical methods (Bhagavantam and Venkatarayudu, 1939) to the Bravais cell of smallest size and evaluate the infrared and Raman activity of the possible modes of oscillation and their combinations and harmonics. It is found that the 15 possible modes fall under 8 representations and 4 frequencies are allowed in Raman effect and 4 in the infrared. The selection rules for the infrared activity of the combinations and harmonics permit the following: $A_{1g} \times A_{2u}$; $A_{2u} \times E_g$; $A_{1g} \times E_u$; $A_{2u} \times E_u^2$; $A_{2u}^2 \times E_u$; $E_u \times E_u \times A_{2u}$; $E_u \times E_u \times B_{1u}$, etc.

The vibration spectrum of rutile has been studied by Dayal (1950) and Matossi (1951) utilising the Raman effect data (Narayanan, 1950) and the infrared reflection maxima, observed by Leibisch and Rubens.

Ordinary ray	14·5	16	18·5	39 μ.
Extraordinary ray ..	16	19·3	22·2	30 μ

However polarisation studies (Narayanan, 1953) have brought out the necessity for a reassignment of the frequencies to the different modes. Using the frequencies given in the above paper and also assuming that to a first approximation the frequencies of type E_u, consistent with their known symmetry, to be given by $\nu_{10} = 690$, $\nu_{11} = 540$ and $\nu_{12} = 256$ cm.$^{-1}$ it is possible to give an explanation for the infrared absorption data as shown in Table I.

TABLE I

Observed cm.$^{-1}$	Combination	Calculated cm.$^{-1}$
695	ν_{10}	690
780	$\nu_5 + \nu_6$	774
833	$\nu_6 + 2\nu_{12}$	842
1053	$\nu_6 + \nu_{11} + \nu_{12}$	1126
↓		
1205	$\nu_1 + \nu_{11}$	1150
1524	$\nu_6 + \nu_{10} + \nu_{12}$	1276
1548	$2\nu_1 + \nu_6$	1550
	$\nu_6 + \nu_{10} + \nu_{11}$	1560
1852	$2\nu_1 + \nu_{11}$	1760
	$\nu_8 + \nu_{10} + \nu_{11}$	1766
	$2\nu_1 + \nu_{10}$	1910

It will be seen that though the allowed combinations satisfactorily explain the observed infrared spectrum in regard to the location of the absorptions, agreement of the actual wavelength of the maxima is by no means satisfactory. This is probably due to the inaccurate knowledge of the frequencies of type E_u.

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