

POLYMERS AND NEW INFRARED ABSORPTION
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ABSTRACT

New absorption bands of water at 1.79 and 1.74μ are interpreted as combination bands arising from 510 cm^{-1} (19.5μ) + 1640 (6.1μ) + 3450 (2.90μ) and $510 + 1640 + 3580$ (2.79μ) respectively. The 19.5μ band, although somewhat hypothetical, is assumed to represent the vibration of one H_2O group against another, either in a simple polymer or in a definitely arranged lattice of H_2O groups. The well-known 4.7μ band, which has no parallel in the water vapor spectrum, probably is $(510 + 1640)\text{ cm}^{-1}$. The spectrum of selenite, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, has bands paralleling all of the liquid water bands in the shorter wave region, but all resolved into doublets.

THERE seem to be pronounced tendencies at present for the chemist and the physicist to disbelieve the existence of polymer molecules as definite entities. Thus G. G. Longinescu¹ in a summary article on "molecular association" would explain, through a theory of molar concentration, all of the abnormalities in the behavior of certain liquids usually accounted for through the postulated existence of relatively simple molecular aggregates or polymers. He states, "Solids and liquids are composed of simple molecules just as gases are. Associated molecules do not exist; only the concentration of simple molecules varies from one substance to another and is much greater for 'associated' molecules than for normal compounds." C. P. Smyth² states, "The deviation of various properties of liquids from normal behavior, which many investigators have attributed to the formation of molecular complexes of definite chemical formulae, may be explained in terms of mere orientation of the molecules relative to one another and of the electric forces acting between them. In extreme cases the orientation may become so pronounced and the forces so strong that definite complex molecules are formed." G. W. Stewart has given the name of "cybotactic state" to this supposed condition of orientation or alignment of relatively large numbers of molecules and in the example of water³ he believes his x-ray analysis of the liquid state can be interpreted as vitiating the previous conception of the simultaneous existence of mono-, di- and trihydrol molecules.

In spite of the present tendencies briefly outlined above new spectroscopic findings in the infrared absorption of water and of the water of crystallization in selenite seem to favor the concept of definite polymers. Using the recording quartz spectrograph of moderate dispersion and resolving power which

¹ G. G. Longinescu, *Chem. Rev.* **6**, 381 (1929).

² C. P. Smyth, *Chem. Rev.* **6**, 549 (1929).

³ G. W. Stewart, *Phys. Rev.* **37**, 9 (1931).

has been employed in many previous investigations, two new closely neighboring absorption bands at 1.74μ and 1.79μ have been found for liquid water. Absorbing layers between 0.5 and 2 mm are most suitable for bringing out the bands. These bands apparently escape detection by the visual method customarily used but may be found, as a single unresolved weak absorption maximum in the author's⁴ curve for water published in 1924. It is possible that at that time this maximum was thought to be the atmospheric water vapor band at 1.87μ , although its location is definitely removed from this band. The water vapor band obviously is obscured by the broadening of the 1.98μ liquid band.

The 1.74μ and 1.79μ bands find no place in the interpretation and correlation of the spectrum of the triatomic H_2O molecule. The water vapor molecule is fairly certainly known⁵ to be triangular and should have three fundamental frequencies, although one of these may be weak because of a small change in the electric moment of the molecule produced by the vibration giving rise to it. Only two of the fundamental frequencies can be identified with comparative certainty with the 6.27μ and 2.67μ absorption bands of the vapor. Whether the third fundamental wave-length is "active" and lies in the region $2\text{--}3\mu$, as is believed by Mecke,⁶ must be finally decided by an analysis of the rotational structure of this region. In any event it is impossible to associate the new bands of the liquid at 1.74μ and 1.79μ or the moderately strong band at 4.7μ with this third fundamental for they do not appear in the vapor spectrum. Furthermore, all of the known higher frequencies of the vapor spectrum can be interpreted as harmonics or combinations of the 6.27μ and 2.67μ bands, and all the higher frequencies of the liquid spectrum, excluding the 4.7μ , 1.79μ and 1.74μ bands, can be analogously regarded as harmonics or combinations of 6.1μ and $\sim 3\mu$ fundamentals. Therefore, it seems necessary to look to another entity as the origin of these excluded bands, and the most probable entity is a polymer.

If we assume the existence in the spectrum of the liquid of a band at 19.5μ (510 cm^{-1}) then the 4.7μ (2130 cm^{-1}) may be regarded as the additive combination of 510 and 1640 cm^{-1} (6.1μ). Again, 1.74μ (5750 cm^{-1}) and 1.79μ (5590 cm^{-1}) may be interpreted as combinations of $(510+1640)\text{ cm}^{-1}$ with 3580 cm^{-1} (2.79μ), and $(510+1640)\text{ cm}^{-1}$ with 3450 cm^{-1} (2.90μ) respectively within the limits of accuracy with which the values are known. The bands at 2.79μ and 2.90μ represent two of the three components of the 3μ absorption region revealed through Raman scattering studies by Kinsey⁷ and by others. The 19.5μ band is in a degree hypothetical although such a band has been quoted by Rawlins and Taylor⁸ as present in the spectrum of water. The writer however has been quite unable to find any very clear-cut evidence for the existence of such a band. It is true that the reflection and absorption rec-

⁴ J. W. Ellis, *J.O.S.A.* and *R.S.I.* **8**, 1 (1924) (Fig. 3B).

⁵ See D. M. Dennison, *Rev. of Mod. Physics* **3**, 280 (1931).

⁶ R. Mecke, *Phys. Zeits.* **30**, 907 (1929).

⁷ E. L. Kinsey, *Phys. Rev.* **34**, 541 (1929).

⁸ Rawlins and Taylor, "Infrared Analysis of Molecular Structure," p. 61.

ords of Rubens and Ladenberg⁹ show a gradual rise from about 8μ toward a maximum near 18 or 20μ , at which point their records cease, but whether this is to be identified with the assumed 19.5μ maximum is uncertain. This uncertainty is enhanced by the fact that this general rise parallels an increase in absorption by the vapor, a phenomenon usually ascribed to a complicated rotational spectrum.

A record of a thin film of water has been taken, to ascertain if there is characteristic absorption near 2.5μ , in which region bands representing combinations of 19.5μ with 2.79 and 2.90μ might be anticipated. Although there is pronounced absorption in this region it has been impossible to decide whether it is caused by new bands or whether it is caused by the considerable breadth of the 2.79 and 2.90μ absorption maxima themselves.

In spite of the uncertainty as to whether a 19.5μ band has ever been observed, it is here assumed to exist and is interpreted as arising from the vibration of two H_2O groups against each other. But it seems impossible to determine whether this vibration occurs in a simple dihydrol molecule, H_4O_2 , or between neighboring constituent groups of a more general space lattice. If the former is true the 19.5 , 6.1 , 2.90 , and 2.79μ bands must be looked upon as four of the fundamental bands characteristic of the dihydrol molecule, the last three not differing much from bands characterizing the H_2O vapor molecule. The 4.7 , 1.79 and 1.74μ bands would then be combination bands arising from these fundamentals. If the latter is true these last three bands must be regarded as combinations of a low frequency lattice vibration with characteristic vibrations of the H_2O molecular units. In the terms ordinarily used these would be combinations between "external" and "internal" vibrations of the lattice, a phenomenon which in general is permitted.¹⁰ The latter interpretation would seem to gain support in the fact that the 4.7μ band is even stronger in ice¹¹ than in water; however, it has never been proved that the elementary unit of the ice lattice is not H_4O_2 . It is rather remarkable that the spectrograph used resolved the 1.74 and 1.79μ bands in as much as it does not resolve the harmonics of 2.79 and 2.90μ . In this connection it must be mentioned however that the Raman scattering reveals a third maximum⁷ in the 3μ region, at 3.14μ , which does not seem to play a role in the combination phenomena which we are discussing but which, as a study of temperature variation and the effects of dissolved substances indicate, does have harmonics associated with it. The relative sharpness of the 1.74 and 1.79μ bands does, in the light of the present interpretation, indicate a fairly sharp 19.5μ band and consequently the existence of a more definite attractive force than would be obtained in a mere orientation and alignment of molecules inferred in Longinescu's theory of molar concentration or Stewart's cybotactic state.

Although no study was made of ice in this investigation the variation of absorption with temperature was studied. In addition to the sharpening and shifting of band centers toward shorter wave-lengths, a phenomenon dis-

⁹ Rubens and Ladenburg, *Verh. d. D. Phys. Ges.* **11**, 16 (1909).

¹⁰ Schaefer and Matossi, *Das Ultrarote Spektrum*, p. 287.

¹¹ Tamman, *Naturwiss.* **15**, 632 (1927).

covered by Collins,¹² it was found that the transmission through a 1.5 mm cell in the region 1.74–1.79 μ increased at least 50 percent as the temperature was raised from 8° to 99° C. But the transmission in the region of 1.60 μ increased even more so and consequently it is difficult to say whether the change at 1.74–1.79 μ really represents a diminution in the strength of the characteristic absorption bands there. The decrease in absorption in the 1.60 μ region seems to be associated with a decrease in the longer wave portion of the broad 1.45 μ harmonic band.

The interpretation of the preceding paragraphs is supported by an analysis of the absorption spectrum of selenite, CaSO₄·2H₂O. It has long been known¹³ from a study of reflection and absorption spectra that the water molecules in crystals which have water of crystallization have characteristic frequencies similar to those of water and ice. The well-known water bands near 6, 4.7, 3, 2 and 1.5 μ were found in selenite, or gypsum, by Coblenz.¹⁴ The 3 μ absorption has been resolved into a doublet by Schaefer¹⁵ with components at 2.85 and 2.95 μ . In the shorter wave-length region the present investigation has revealed a doubleness in the following bands, the first four of which have been previously recorded by the writer⁴: 1.99, 1.95 μ ; 1.74, 1.70 μ ; 1.50, 1.45 μ ; 1.20, 1.17 μ ; 1.02, 0.98 μ . All of these bands closely parallel bands in water, as a reference to Table I and Fig. 1 will reveal, although some

TABLE I. Wave-lengths and wave numbers for water and selenite.

Interpretation	Selenite		Water	
	λ	ν	λ	ν
ν^*	14 μ	715 cm ⁻¹	19.5 μ	510 cm ⁻¹
ν_1	6.1	1640	6.1	1640
$\nu^* + \nu_1$	4.3	2320	4.7	2130
ν_2	2.95	3390	2.90	3450
ν_3	2.85	3510	2.79	3580
$\nu_1 + \nu_2$	1.99	5020	} 1.96	5050
$\nu_1 + \nu_3$	1.95	5130		
$\nu^* + \nu_1 + \nu_2$	1.74	5750	1.79	5590
$\nu^* + \nu_1 + \nu_3$	1.70	5880	1.74	5750
$2\nu_2$	1.50	6670	} 1.45	6850
$2\nu_3$	1.45	6900		
$\nu_1 + 2\nu_2$	1.20	8340	} 1.18	8480
$\nu_1 + 2\nu_3$	1.17	8550		
$3\nu_2$	1.02	9800	} 0.98	10200
$3\nu_3$	0.98	10200		

of them were differently interpreted in the earlier publication.⁴ It is interesting to note that there is greater sharpness in the selenite bands, resulting in a resolution not only of the 1.74, 1.70 μ maxima but of all of the simpler overtones and combination bands. The 2.95, 2.85 μ ; 1.50, 1.45 μ and 1.02, 0.98 μ doublets form an anharmonic series with doublet separations increasing in the following manner: 120, 230 and 400 cm⁻¹. The 1.99, 1.95 μ and 1.20, 1.17 μ

¹² J. R. Collins, Phys. Rev. **26**, 771 (1925).

¹³ For a summary see Schaefer and Matossi, reference 10.

¹⁴ See reference 13, p. 363.

¹⁵ See reference 13, p. 368.

maxima represent combinations of 6.1μ with 2.95 , 2.85μ and 1.50 , 1.45 respectively. The 1.99 , 1.95μ and 1.20 , 1.17μ doublets have wave number separations of 110 and 210 cm^{-1} , in good agreement with the separations of the bands which govern them.

Of particular interest, however, is the 1.74 , 1.70μ doublet corresponding to 1.79 , 1.74μ of pure water. Since it represents a combination of $(2.95, 2.85\mu)$, and 6.1μ with a still greater wave-length, the value of this greater wave-length can be determined. It turns out to be about 14μ , considerably lower

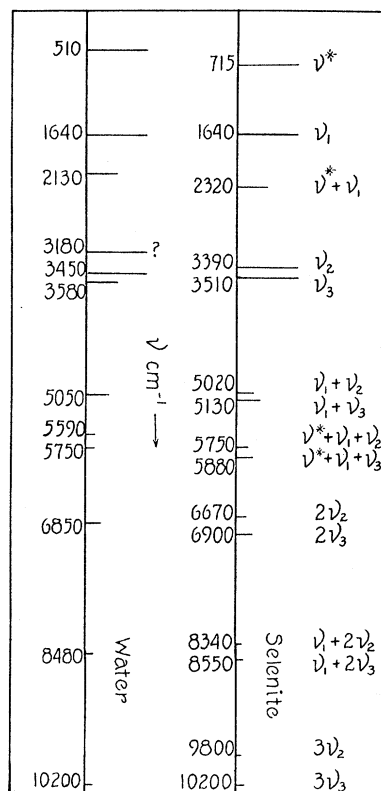


Fig. 1. Wave number diagram.

than the corresponding 19.5μ band of water. But this is consistent with the assignment by Schaefer and Matossi of a band at about 14μ in the reflection spectrum of gypsum¹⁶ to the water of crystallization. The 715 cm^{-1} frequency of the 14μ band is here regarded as the vibration of one H_2O group against another, this frequency differing from that of the corresponding 510 cm^{-1} frequency in ordinary water because of differences in the perturbing influences of surrounding molecules or ions.

Schaefer and Matossi¹⁷ point out from an analysis of Coblenz's records

¹⁶ See reference 13, p. 334; also Fig. 135, p. 331.

¹⁷ See reference 13, p. 363.

for selenite, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and for anhydrite CaSO_4 , that the 4.7μ region of absorption represents a superposition of a water band and the first overtone of a 9μ band characteristic of the SO_4 ion. It is clearly evident that the wave-length of the water band is the shorter of the two, at such a wave-length as to yield with the SO_4 overtone band a maximum at 4.5μ . This fact is in good agreement with the present interpretation of this band being a combination of 14μ with 6.1μ .

The wave-length and wave-number data, both for liquid water and the water of crystallization in selenite, have been assembled in Table I. A wave number diagram has also been drawn to scale in Fig. 1; however, the intensities of various bands, represented by heights of lines, are for the most part quite arbitrary.