Infra-Red Absorption Spectra of the Water Molecule in Crystals

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The paper reports the absorption spectra taken under high resolution and dispersion near 3μ which are produced by water in various bound states in certain crystals and indicates the modes of vibration which cause the observed bands. Bands in sodium bromide, $NaBr \cdot 2H_2O$, extending from 3 to 2μ, and bands near 2.5μ in sodium iodide, $NaI \cdot 2H_2O$, and barium chloride, $BaCl_2 \cdot 2H_2O$, are reported and discussed. The absorption of beryl, mica, topaz, and quartz from 2 to 3μ is also studied. It is concluded that bands in beryl, which are strikingly similar to bands of water dissolved in carbon tetrachloride, are caused by monomeric water, or vapor-like molecules, in solid solution in the open crystal lattice of beryl. In mica, it is concluded, only bound hydroxyl groups are present. The evidence indicates that both bound hydroxyl groups and highly perturbed coordinated water exist in topaz. In fused quartz there is evidence for the existence, in some samples, of water in solid solution.

THE purpose of this paper is to report the absorption spectra taken under high resolution and dispersion near 3μ which are produced by water in various bound states in certain crystals, and to indicate the modes of vibration which cause the observed bands.

It is well known that the water bands are quite sensitive to the environment of the water molecule, being modified or perturbed in characteristic fashion by change of state and by solution in various solvents. The relatively inhomogeneous structure of liquid water and ice, however, so broadens the bands and destroys the structure to such an extent that little information regarding the nature of the perturbation is furnished by them. The band structure shown by water in carbon tetrachloride under moderate dispersion in the 1.4μ overtone region,[1] and in the 3μ region[2] under high dispersion and resolution suggested the advisability of examining water bound in crystals as water of crystallization in solid solution, with a grating spectrometer of high resolution. Bound water in crystals absorbs radiation in a far more homogeneous environment than in ice or liquid water, particularly in hydrates of simple structure and with a minimum number of molecules of hydration. Bound water in crystals should be

perturbed in a more regular manner, and show a distinct and simple band structure.

In this paper bands in sodium bromide, $NaBr \cdot 2H_2O$, extending from 3 to 2μ, and bands near 2.5μ in sodium iodide, $NaI \cdot 2H_2O$, and barium chloride, $Ba Cl_2 \cdot 2H_2O$, are reported and discussed, so far as we know, for the first time. In addition the absorption in the 2 to 3μ region of beryl, mica, topaz, and fused quartz studied previously only under low dispersion is obtained under the high resolution of an echelette grating spectrometer, and is discussed.

THE SPECTROMETER

The instrument used in this study is an echelette grating spectrometer of high resolution and dispersion for the $2-4\mu$ wave-length region with an optical arrangement which is shown in Fig. 1. The echelette grating has 5000 lines to the inch with rulings 11.0 cm long extending over a
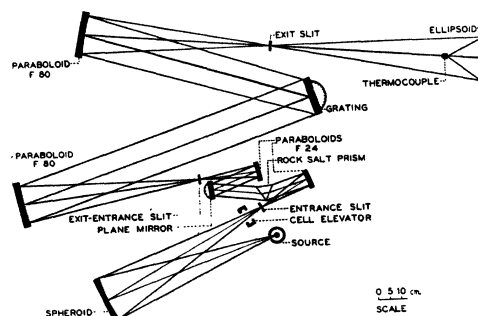

FIG. 1. Infra-red absorption spectra of water molecule in crystals.

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[1] E. L. Kinsey and J. W. Ellis, Phys. Rev. **51**, 1074 (1937); **54**, 599 (1938).
[2] J. Fox and A. Martin, Proc. Roy. Soc. **A174**, 234 (1940).

a distance of 16.5 cm and was one of the first aluminum on glass echelettes ruled by R. W. Wood at The Johns Hopkins University. The Pyrex glass blank is 8 inches in diameter. The diamond of the ruling engine was set to give concentration in the first order at 3μ. Two paraboloidal mirrors 8 inches in diameter and of 80-cm focal length collimate the radiation. A 60° rocksalt fore-prism removes the overlapping higher orders and an ellipsoidal mirror concentrates the radiation on the thermocouple. The bismuth-tin, bismuth-antimony thermocouple is connected to a Leeds and Northrup high sensitivity galvanometer which works on an eleven-meter light arm by means of a diffraction edge from a lamp filament reflected in the galvanometer mirror. The entire spectrometer is housed in a metal chamber in which the water vapor content of the enclosed air is maintained below 10^{-3} mg of water per liter.

The Rayleigh resolving power is 0.9A and the practical resolving power is about 5A. In the crystal work described here this resolution was not utilized. Exit and entrance slit widths corresponding to a spectrum spread of 15A were used. Since the angle through which the grating is rotated from a given fiducial position determines the wave-lengths of the radiation falling upon the exit slit, the accuracy of the wave-length measurement is governed by the accuracy with which this angle can be read. For a wave-length accuracy equal to the Rayleigh resolving power (0.9A) the angle reading must be accurate to within 2 sec. The angle is measured by an optical method rather than by means of an accurately divided circle. A small optically flat mirror is mounted on the grating axis so that the plane of the mirror contains the line of centers of the cone axis of the grating mounting. A telescope views the image, formed by the mirror, of a one-meter steel scale mounted on a heavy steel bracket bolted to a concrete wall. Steel clamps conform the steel scale to the arc of a circle (5.3-meter radius) whose center lies on the grating axis. The telescope has an achromatic objective 6 cm in diameter, and is held in a rigid mounting on a large concrete pillar 4 meters distant from the grating. Three alignment errors are present and affect the accuracy of the wave-lengths: (1) error in the position of the center of curvature of the
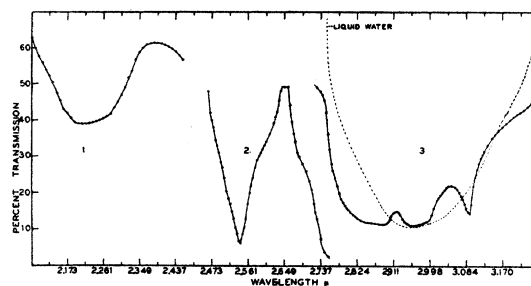

Fig. 2. The absorption of $NaBr \cdot 2H_2O$.

scale; (2) error in the position of the plane mirror on the grating axis; and (3) error in the alignment of the telescope axis through the axis of rotation of the grating. These three errors can be controlled to guarantee an accuracy of 0.9A in wave-length measurements. The fifth and sixth orders of the strong emission lines of a mercury arc were used to calibrate the grating scale.

WATER IN SODIUM AND BARIUM HALIDES

The absorption of sodium bromide, $Na Br \cdot 2H_2O$, in the $2.1–3.1\mu$ region is shown in Fig. 2. Since the intensity of absorption varies widely in this range, it was necessary to vary the thickness of the crystal in use to show the bands to advantage. Region 1 near 2.2μ shows the absorption of a crystal 0.011 cm thick, and region 2 near 2.5μ shows the absorption of a crystal 0.0057 cm in thickness. Region 3 near 3.0μ is a region of such very intense absorption that a film remaining on a microscope slide cover-glass which has been dipped into a saturated solution of sodium bromide was used to obtain its spectrum. The film is still too thick to show all the possible structure.

The central component of the 3μ band, region 3 of Fig. 2, lies at approximately 3380 cm^{-1} (2.95μ) and is assumed to be the fundamental symmetric vibration mode ν_π. The other broad band extending from approximately 3453 to 3561 cm^{-1} with center near 3510 cm^{-1} is assigned as the asymmetric vibration mode, ν_σ. This assignment causes ν_π to shift by 65 cm^{-1} to a lower frequency from its position in liquid water and ν_σ to shift by 70 cm^{-1} in a similar fashion. These shifts are based upon a reasonable assignment of the bands in liquid water discussed in the following para-

graph. Frequency shifts in the liquid water bands in this region caused by cooling and principally by a change of state to ice show that frequencies are lowered as the lattice field becomes more homogeneous, and one would expect to find what this assignment shows, that the frequencies are lowered in the more homogeneous crystal lattice of NaBr·2H₂O.

In liquid water the correlation of absorption maxima with the symmetric (ν_π) and antisymmetric (ν_σ) modes of vibration, which is usually accepted, is very questionable. Fox and Martin,[2] and others, have regarded the maximum near 2.94μ (3403 cm⁻¹), which is observed in the infra-red, as the asymmetric mode ν_σ and have taken the band, which occurs in the Raman effect near 2.90μ (3445 cm⁻¹), as owing to the symmetric ν_π vibration. This assignment requires rather unequal shifts in frequency for ν_σ and ν_π with change of state (liquid to vapor) and with change in environment (solution in carbon tetrachloride), ν_σ shifting by 353 cm⁻¹ from liquid water to vapor, and ν_π by 209 cm⁻¹. ν_σ shifts by 302 cm⁻¹ and ν_π by 169 cm⁻¹ in passing from the spectrum of water in carbon tetra-

TABLE I. Frequency differences for water in various states.

Frequency difference	Water vapor	Water in CCl₄	Liquid water	NaBr·2H₂O
$\nu_\sigma - \nu_\pi$	102 cm⁻¹	91 cm⁻¹	135 cm⁻¹	130 cm⁻¹
$\nu_{\pi R} - \nu_\pi$				445
$\nu_{\sigma R} - \nu_\sigma$			396	424
$\nu_{hR} - \nu_h$				496

TABLE II. Comparison of assignments.

Assignment	Water in CCl₄	Liquid Water	NaBr·2H₂O	Ice
ν_R		440ᵃ–500ᵇ cm⁻¹		601ᵃ cm⁻¹
"Dihydrol" ν_h		3219ᵃ (3.106μ)	3229 cm⁻¹ (3.093μ)	3136ᵃ (3.19μ)
ν_π	3614 cm⁻¹ (2.767μ)	3445ᵃ (2.90)	3380 (2.959)	3330ᵃ (3.003)
ν_σ	3705 (2.699)	3580ᶜ (2.79)	3510 (2.849)	
$\nu_{hR} = \nu_h + \nu_R$			3725±20 (2.670–2.699)	
$\nu_{\pi R} = \nu_\pi + \nu_R$			3825±20 (2.631–2.605)	
$\nu_{\sigma R} = \nu_\sigma + \nu_R$		3976ᵈ (2.515)	3934 (2.542)	
$\nu_\pi + 2\nu_R$ $\nu_\sigma + 2\nu_R$			4350–4610 (2.30–2.19)	

ᵃ See reference 6.
ᵇ See reference 8.
ᶜ See reference 3.
ᵈ See reference 1.

FIG. 3. Absorption of: A, BaCl₂·2H₂O; B, NaI·2H₂O.

chloride to the spectrum of liquid water. In fact, ν_π lies on the short wave-length side of ν_σ in liquid water and on the long wave-length side of it in water vapor and in water in carbon tetrachloride. Since both ν_σ and ν_π are valence vibration frequencies and are mainly determined by the O − H bond force constant, these changes of environment ought to produce shifts in ν_π and ν_σ which are not very different. If, however, we identify the Raman band in liquid water at 3580 cm⁻¹ as ν_σ, as Ellis[3] did in 1931, and regard the Raman band at 3445 cm⁻¹ as ν_π, the frequency shifts of the two fundamental modes are more nearly the same. Table I, giving the difference $\nu_\sigma - \nu_\pi$ for water in various states, shows that the variations for different environments including water in sodium bromide are not large. If the assignment of Fox and Martin is used, one of the sodium bromide bands (3510 cm⁻¹) would have a higher frequency than in liquid water, a circumstance which is not likely (the water being more highly coordinated in the crystal), and the difference $\nu_\sigma - \nu_\pi$ would be 42 cm⁻¹ for liquid water as compared with 130 cm⁻¹ for NaBr ·2H₂O. The infra-red band at 2.94μ in liquid water is a composite being a superposition of ν_π, ν_σ, and a frequency ν_h which appears only in ice, crystals, and as a Raman band (3219 cm⁻¹) in liquid water. The large frequency shifts observed in the 2.94μ band with temperature change, which have in the past been attributed to frequency changes in ν_σ are more likely caused by changes in the relative intensity of its com-

[3] J. W. Ellis, Phys. Rev. 38, 693 (1931).
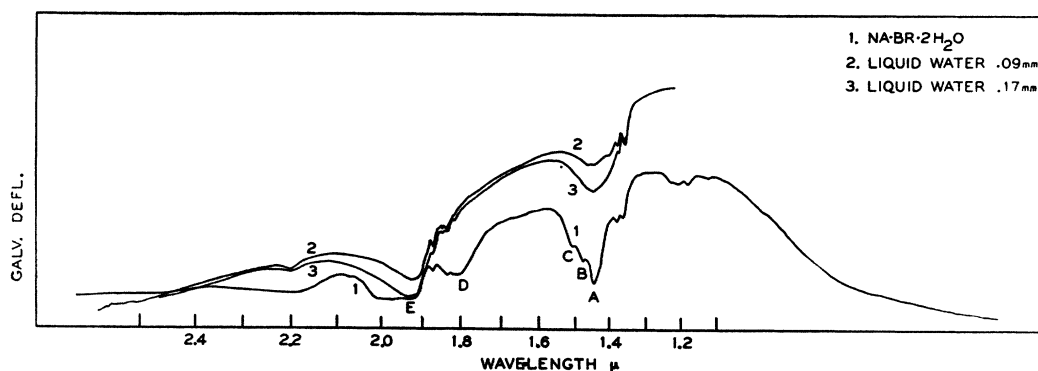
FIG. 4. Spectrum of $NaBr_2 \cdot 2H_2O$ and liquid water.

ponents (cf. Cross, Burnham, and Leighton's[4] work on the Raman effect). Where there is little or no overlapping, as in the Raman band ν_h at 3.14μ (3221 cm^{-1}), temperature has little effect upon the frequency. This latter band, which is weakened by a rise in temperature and by dilution of the water with nitric acid, is caused undoubtedly by polymerization, due as Bernal and Fowler[5] have suggested to the persistence of tridymite-ice-like water. Because it appears in $NaBr \cdot 2H_2O$ we will speak of it as the "dihydrol" band. In water vapor ν_σ is predominantly strong and the "dihydrol" band is missing. For water

TABLE III. Interpretation of bands near 2.52μ.

Assignment	BaCl₂·2H₂O	Δν	NaBr·2H₂O	Δν
"Dihydrol"	3280 cm^{-1} R^a		3229 cm^{-1}	
		546		496
"Dihydrol"+ν_R	3775		3725	
ν_π	3340 R^a		3380	
		519		445
$\nu_\pi+\nu_R$	3839		3825±20	
ν_σ	3450 R^a		3510	
		552		424
$\nu_\sigma+\nu_R$	4002		3934	

R: Raman band.
a See reference 7.

TABLE IV. NaBr·2H₂O bands.

Bands in Fig. 4	Assignment	Computed value
A. 6896 cm^{-1}	$\nu_\pi+\nu_\sigma$	6890 cm^{-1}
B. 6748	ν_σ+Dihydrol	6739
C. 6631	ν_π+Dihydrol	6609

[4] Cross, Burnham, and Leighton, J. Am. Chem. Soc. 59, 1134 (1937).
[5] J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).

in carbon tetrachloride ν_π and ν_σ are both strong; ν_h is still missing. In liquid water ν_σ, ν_π, and ν_h are all present with ν_h and ν_π strong. In ice ν_π and ν_h are strong and ν_σ is weak or missing. ν_σ is not found in the Raman spectrum of ice.

The third and long wave-length component of the 3μ band of sodium bromide is of less intensity than the other two but quite sharp. It lies in the region of the first overtone of the deformation vibration ν_δ (1645 cm^{-1}). Since no pure harmonic bands have been observed for ice or liquid water, it is more likely to be the dihydrol frequency which falls in liquid water at 3219 cm^{-1}, and in the sodium bromide at 3229 cm^{-1}. Table II compares the assignments for water in sodium bromide with the assignments for liquid water, water in carbon tetrachloride and ice. The frequencies in this region decrease in the order: vapor (with bands at $\nu_\sigma = 3656^2$ and $\nu_\pi = 3654$),[6] water in carbon tetrachloride, water in sodium bromide, ice.

Two Raman bands observed by Nayar[7] for sodium bromide indicate the existence of two frequencies in the 3μ region, but they are not likely to be the ν_π and the ν_σ bands reported here in the infra-red. They fall at 3430 cm^{-1} (2.915μ) and 3570 cm^{-1} (2.801μ) on either side of the broad band at 3510 cm^{-1}. They are apparently components of ν_σ.

The 2.52μ (3934 cm^{-1}) band in $NaBr \cdot 2H_2O$ given in Fig. 2 shows the sharpening and the intensity increase characteristic of the behavior of water bands under crystal lattice or solution perturbation. The molecular extinction coef-

[6] J. H. Hibben, J. Chem. Phys. 5, 166 (1937).
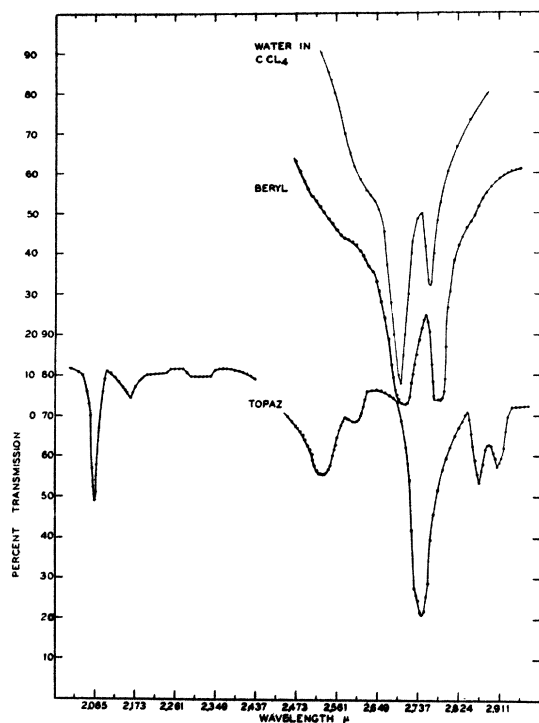[7] P. G. N. Nayar, Proc. Ind. Acad. Sci. A8, 479 (1938).

FIG. 5. Band of water in silicates and in CCl₄.

ficient at maximum absorption increases from 0.46 (Fox and Martin[2]) to about 2.0. In liquid water the band falls at 3976 cm⁻¹ as measured by Fox and Martin. It is interpreted as the combination of the asymmetric vibration ν_σ and a frequency of hindered rotation, ν_R.[8] There are evidences of two other bands which appear as shoulders, one at 3820 cm⁻¹, approximately, and the other approximately at 3713 cm⁻¹. The three bands—the deep band, and these two shoulders—are separated from the three frequencies ν_σ, ν_π, and ν_h by 424, 450, and 490 cm⁻¹, respectively, indicating that the three bands may be combinations of the fundamental frequencies with a frequency of hindered rotation around 450 cm⁻¹.

It is of interest to compare the NaBr·2H₂O bands in this region with those of a barium chloride (BaCl₂·2H₂O) and a sodium iodide (NaI·2H₂O) crystal. In the 2.52μ region, shown in Fig. 3, structure appears for barium chloride consisting of one fairly strong band at 4002 cm⁻¹ (2.499μ) and two weaker bands at 3839 cm⁻¹

(2.605μ), and 3775 cm⁻¹ (2.649μ). Table III gives an interpretation for these bands. The sodium iodide band falls at 3918 cm⁻¹ (2.552μ) quite close to the bromide band at 3934 cm⁻¹ (2.542μ), but no structure appears because of the excessive thickness of the crystal sample (0.02 cm).

Sodium bromide has a broad band at 2.271μ (4510 cm⁻¹). There is no counterpart to this band in liquid water. It falls in the region of a combination of the valence vibrations and the first overtone of a hindered rotation in the neighborhood of 450 to 500 cm⁻¹ ($\nu_\sigma + 2\nu_R = 3510 + 1000$).

The authors are indebted to Professor Joseph W. Ellis for data on the combination bands of NaBr·2H₂O in the 1 to 2.3μ region. Professor Ellis took the spectrum of NaBr₂·2H₂O on his quartz-prism, self-recording spectrometer, and obtained the spectrum shown in Fig. 4. The 1.44μ ($\nu_\sigma + \nu_\pi$) band of liquid water is shifted to a longer wave-length for the coordinated water in the crystal, where it has developed three components. Table IV lists the three components of the 1.44μ band, and suggests an interpretation. The relative intensities of the three components support the assignment chosen. The 1.79μ ($\nu_\sigma + \nu_\delta + \nu_R$) band (D in Fig. 4) is much more intense for coordinated water than for liquid water. This increase is in agreement with the increase found for the hindered rotation band at 2.52μ. Figure 4 shows the broad absorption region at 2.2μ, which was also obtained on the grating spectrometer. The band marked E in Fig. 4 is the $\nu_\sigma + \nu_\delta$ band at 1.93μ.

WATER IN SILICATES

The 3μ infra-red absorption spectra of silicates offer interesting information on the behavior of water in the silicate crystal structure. The O − H bands are apparently produced in various ways, e.g., by water in solid solution, by an hydroxyl group in the silicate structure, and by coordinated water of crystallization. Matossi and Bronder[9] have analyzed the many absorption and reflection bands of beryl (aquamarine) from 1.3μ to 10μ with an instrument of low resolving power, and have accounted for the fundamental and

[8] C. H. Cartwright, Phys. Rev. 49, 470 (1936).

[9] F. Matossi and O. Bronder, Zeits. f. Physik 111, 1 (1938).

combination frequencies of the silicate radical. A band near 2.7μ, however, is questionable. Matossi and Bronder tentatively assign it to an hydroxyl group. They point out that water can be present in this silicate to the extent of 1 percent, whereas the intensity of the band indicates an impurity of 5 to 10 percent. We obtained the band under the high resolution of the grating instrument and present it in Fig. 5. The band is strikingly similar in structure and position to the band obtained for water in carbon tetrachloride, a fact which suggests an interesting and curious cause for it. The centers of the two bands in beryl fall at 2.710μ (3690 cm^{-1}) and 2.780μ (3598 cm^{-1}) as compared to 3705 cm^{-1} and 3614 cm^{-1} for water in carbon tetrachloride. In the beryl band a shoulder appears on the short wavelength side similar to that for water in carbon tetrachloride. This correlation suggests that the 3690 cm^{-1} band is the envelope of the enhanced Q lines of ν_σ for the water molecule; the 3597 cm^{-1} band is ν_π, and the shoulder is the envelope of the R lines of ν_σ. Beryl is a silicate with rings of linked tetrahedra (Be$_3$Al$_2$Si$_6$O$_{18}$), and is an elegant structure composed of hexagonal rings made of six silicon-oxygen tetrahedra (W. L. Bragg).[10] The aluminum and beryllium atoms bind these rings into a coordinated structure, such that each aluminum atom lies in a sixfold group. The structure does not offer a place for a bound hydroxyl group as does the structure of topaz or mica, but the hexagonal rings produce large open channels, 4.2A across in the beryl structure. The existence of water monomers in this open structure seems possible and would account for the spectrum obtained. An hydroxyl group bound to aluminum gives a single band near 3640 cm^{-1}, e.g., in mica. Beryl does not show this band. It seems, therefore, that monomeric, i.e., vapor-like water exists in solid solution in beryl with beryl acting as an "inactive" solvent like carbon tetrachloride.

Matossi and Bronder[9] find an intense absorption band for muscovite (common mica) near 2.75μ, and assign this band to the hydroxyl group in the mica structure, K Al$_2$(Al Si$_3$ O$_{10}$) (OH)$_2$. Figure 6 shows this band under high resolution (thickness of mica sample 0.0075 mm). The band

center lies at 2.747μ (3641 cm^{-1}). The weak uniform bands appearing at regular intervals are probably caused by interference in the mica film, since these small bands vary with the thickness of different mica samples. The strong hydroxyl band lies at a frequency common to other compounds containing an O$-$H group, e.g., ethyl alcohol in carbon tetrachloride. In muscovite the O$-$H group is linked to the aluminum atom with no links between O$-$H groups. Each O$-$H, therefore, is a monomer acting as an O$-$H oscillator located in the open mica structure (cf. Bragg and Pauling).[10, 11]

Matossi and Bronder[9] find evidence for water in topaz, (AlF)$_2$SiO$_4$, but find the complex spectrum in the 2 to 3μ region unintelligible. They explain the many bands as due to O$-$H groups under various types of binding in the topaz structure. The 2–3μ spectrum under high resolution (Fig. 5) suggests a more explicit assignment than that of these authors. The sample used was not sufficiently large to cover the entire entrance slit of the spectrometer; the
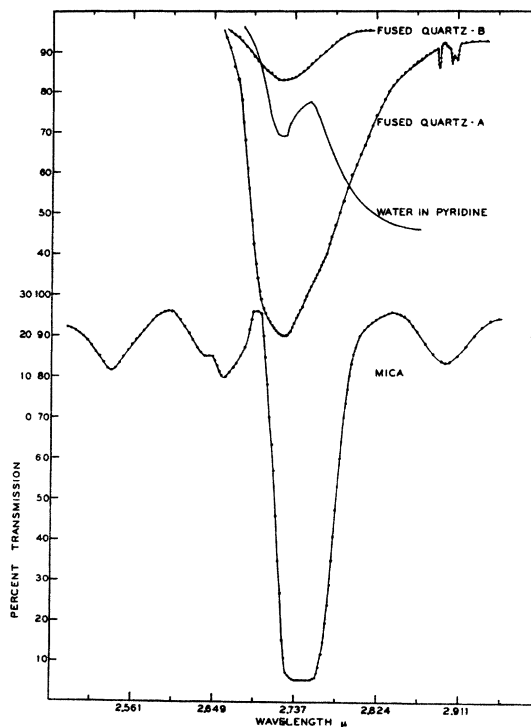

FIG. 6. Absorption in mica and quartz.

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[10] W. L. Bragg, *Atomic Structure of Minerals* (1937).

[11] L. Pauling, *Nature of the Chemical Bond* (1940).

absorption bands should, therefore, be much deeper than indicated (thickness of sample 0.05 cm). An intense band is found at 2.745μ (3643 cm^{-1}), which undoubtedly must be caused by a bound O−H group as in mica (mica 3641 cm^{-1}). Topaz is an aluminosilicate, and a bound hydroxyl is possible, even probable, in its structure. The fluorine atoms of the conventional topaz structure may be partly replaced by O−H groups (cf. Bragg).[10] When an O−H group replaces a fluorine atom it is bound to an aluminum atom in a manner similar to the linkage in mica. The remaining, less intense, absorption bands of topaz occur near the positions of bands in liquid water and in sodium bromide, and suggest the possibility of structural or coordinated water in the open topaz lattice under considerable perturbation. It is attractive, for example, to interpret the doublet at 2.906μ (3441 cm^{-1}) and 2.867μ (3488 cm^{-1}) on the long wave-length side of the O−H band as ν_π and ν_σ. But the difference in wave numbers is only 47 cm^{-1} as compared with 102 cm^{-1} for water vapor, 135 cm^{-1} for liquid water, and 130 cm^{-1} for water in sodium bromide. It may be, on the other hand, that the ν_σ mode splits into a doublet under the perturbing crystal field. ν_π would then lie toward longer wave-lengths in a region not yet investigated (under high resolution) for topaz. Table V gives the suggested, but questionable, assignments. A narrow band at 2.086μ (4793 cm^{-1}) may be a combination band of the O−H fundamental and that of a Si O$_4$ group; e.g., Matossi and Bronder[9] suggest the combination of the O−H vibration (3643 cm^{-1}) and the first overtone of a fundamental frequency of the SiO$_4$ group at 600 cm^{-1}. It is suggested that in addition to a bound O−H group, coordinated water is present in topaz, but not monomeric water as in beryl. The 2.53μ band $(\nu_\sigma+\nu_R)$ and the 2.60μ band $(\nu_\pi+\nu_R)$ indicate a hindered rotation for these proposed water groups in the topaz structure.

WATER IN FUSED QUARTZ

The absorption spectrum of fused quartz has been studied for many years, and a band at 2.72μ is of particular interest. In 1929 Parlin[12] studied

its absorption as a function of temperature, and attributed the band at 2.72μ to a combination of two frequencies of the SiO$_2$ molecule. In the same year Plyler[13] studied the absorption of crystalline quartz and reported a band of very low intensity at 2.72μ, which he regarded as the second overtone of a fundamental frequency at 9μ. Drummond[14] in 1934 found that the 2.7μ band is absent in some specimens of fused quartz and of varying intensity for other specimens. This wide variance of intensity suggested to Drummond that the 2.72μ band is caused not by SiO$_2$, but by an impurity, namely, dissolved CO$_2$. He made a study of the spectrum of fused and crystalline quartz from 1μ to 8μ in 1936.[15] Ellis and Lyon[16] attributed the 2.72μ band to water vapor as the impurity.

The process of manufacture of fused quartz has apparently changed during the past three decades, inasmuch as older specimens exhibit the 2.72μ band, whereas later specimens do not, as illustrated in Fig. 6. The older specimen A is 2 mm thick, and the newer specimen B, is 4 mm thick. The center of the band lies at 2.723μ (3672 cm^{-1}). Figure 6 compares the absorption by fused quartz with that by 0.5 percent water dissolved in pyridine (data from Errera, et al.).[17] Pyridine is an active solvent perturbing the water molecule by a linkage between the

TABLE V. Water bands in topaz.

Assignment	Liquid water	Topaz	$\Delta\nu$
ν_π	3445 cm^{-1} 2.90μ	3441 cm^{-1} 2.906μ	
			404 cm^{-1}
$\nu_\pi+\nu_R$		3845 2.601	
ν_σ?	3580 2.79	3488 2.867	
			464
$\nu_\sigma+\nu_R$	3976 2.515	3952 2.530	
Bound OH		3643 2.745	

[13] E. K. Plyler, Phys. Rev. 33, 48 (1929).
[14] D. G. Drummond, Nature 134, 739 (1934).
[15] D. G. Drummond, Proc. Roy. Soc. 153, 318 (1936); Nature 138, 248 (1936); and 139, 70 (1937).
[16] J. W. Ellis and W. Lyon, Nature 137, 1031 (1936), and 139, 70 (1937).
[17] Errera, Gaspart, and Sack, J. Chem. Phys. 8, 63 (1940).

[12] W. A. Parlin, Phys. Rev. 34, 81 (1929).

nitrogen of the pyridine and the hydrogen of water. The band for water in pyridine lies at 2.719μ (3678 cm^{-1}). For water in carbon tetra-chloride (an inactive solvent) a double band, (ν_σ, 3705 cm^{-1} and ν_π, 3614 cm^{-1}) is found, but for water in pyridine ν_π is not found. The band in fused quartz is at a somewhat higher frequency than is found for hydroxyl groups bound to an atomic structure, namely, 3600 to 3400 cm^{-1} (cf.

Pauling[11] or, for example, the 3643 cm^{-1} O−H band in mica). It is suggested that the 2.72μ band in fused quartz is due to water in a solid, closely-packed solution perturbed by the oxygens of the Si O$_2$ group. Water appears to be more probable than carbon dioxide as an impurity in view of the studies on silicates, and since the 2.72μ band does not show the double structure characteristic of CO$_2$ in this region.

On the Large Scale Distribution of Matter in the Universe

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The following considerations represent an attempt to analyze those effects which govern the large scale distribution of matter in the universe. It is proposed to discuss the problems of: (a) the frequency of occurrence of *clusters of nebulae* which contain different numbers of nebulae, (b) the relative numbers of *nebulae* in dependence of their intrinsic luminosity and mass, and (c) the frequency distribution of various types of *stars* in dependence of their mass and intrinsic luminosity. It is found observationally that clusters of nebulae become the more frequent the fewer nebulae they contain. On the other hand the data so far available indicate that the luminosity function for nebulae exhibits a frequency maximum at the absolute magnitude $M_0 = -14.2$. Reasons are advanced which suggest that this result which was obtained from the purely observational approach to the problem of the general distribution of matter cannot be final. The theoretical analysis of the frequency distribution of various types of stars is largely complicated because of the interference of effects due to light pressure and the generation of energy through subatomic processes and cannot at the present be carried through. The analogous problems for the nebulae and the clusters of nebulae, however, lend themselves to a simple qualitative analysis which, starting from the assumption of a stationary universe, makes use of the principle of the conservation of energy, the virial theorem and the application of statistical considerations to distributions of the Boltzmann and the Smoluchowski types. The results obtained are in good agreement with the observed distribution of the clusters of nebulae. In addition an understanding is arrived at of the important fact that the velocities of field nebulae on the average are only about half as large as those of cluster nebulae. The theoretical considerations given, however, are in *complete contradiction with the luminosity function now generally adopted for the nebulae inasmuch as the existence of a large number of intrinsically faint nebulae* representing more than half of all of the matter in the visible universe *is predicted* which to date must have been overlooked. On the basis of this prediction various criteria are developed to facilitate the discovery of intrinsically faint stellar systems and a systematic search for such systems utilizing the 18-inch Schmidt telescope on Palomar Mountain is described. On the basis of the results achieved so far it is shown that the new distribution function of nebulae in the so-called local group of nebulae deviates markedly in the direction of the theoretical expectations from the luminosity function derived by previous observers. Practical methods are discussed, the application of which should make possible the construction of a more representative distribution function for nebulae over a large range of luminosities. In the final section some of the known observational facts are briefly reviewed which favor the assumption of a stationary rather than an expanding universe.

A. STATEMENT OF THE PROBLEM

ONE of the most conspicuous aspects of the distribution of matter in space lies in the existence of a great variety of types of condensations. Starting from the elementary particles, conglomerations of ever increasing dimensions and material content may be found until we arrive by the way of the stars and the stellar systems (or the nebulae) at the clusters and clouds of nebulae which at the present time are the largest known aggregations of matter which possess individual characteristic structures.

We shall here be concerned with the analysis of the *frequency distribution of various types of large scale condensations of matter*. So far the so-called purely *observational approach* has been made use