

THE HYDROXYL FREQUENCY IN THE RAMAN SPECTRA OF ACIDS AND ACID SALTS.

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1. Introduction.

IN several previous communications by the author, it has been shown from the study of the Raman effect that strong inorganic acids undergo progressive dissociation in aqueous solutions. A typical case is that of nitric acid.¹ In very concentrated solutions of this acid, the Raman lines attributed to the undissociated molecule, HNO_3 , are the most prominent and the lines due to the product of dissociation, NO_3 ion, are very weak. As the concentration falls, the HNO_3 lines decrease and the NO_3 lines increase in intensity. A similar effect due to dilution has been observed on the Raman spectra of iodic, sulphuric, selenic, selenious, phosphoric,² and arsenic³ acids and are explained as due to successive and continuously increasing ionisation of the acid molecules.

Recently, Martin and his collaborators⁴ have studied the Raman effect in a large number of strong electrolytes with a view to discover any line characteristic of the cation-anion oscillations and determine their degree of dissociation in concentrated solutions. These authors found, in agreement with the conclusions of the earlier workers, that no line is present in those electrolytes, which could be definitely attributed to the cation-anion binding. In the case of 100 per cent. sulphuric acid and chloroacetic acid they were unable to record any band characteristic of the O-H group and therefrom they were led to conclude that these acids are completely ionised even in the concentrated solutions and the anomalous variation in the number and the intensity of the Raman lines in them with dilution has to be attributed

¹ Ramakrishna Rao, I., *Proc., Roy. Soc., (A)*, 1930, 127, 279; Woodward, L. A., *Phy. Zeit* 1931, 32, 690.

² Venkateswaran, C. S., *Proc. Ind. Acad. Sci., (A)*, 1935, 2, 119; 1936, 3, 25, 307 and 533.

³ Fehrer, F., and Morgenstern, G., *Zeit. f. Anorg. u. Allg. Chem.*, 1937, 232, 169.

⁴ Bernstein, H. J., Romans, R. G., Howden, O. H., and Martin, W. H., *Trans. Roy. Soc., Canada*, 1936, 30, 49.

not to progressive dissociation but to the various degrees of hydration of the ions or to the existence of other molecular forms in solution.

Further, in a recent contribution to the study of the structure of the acids of phosphorus, Simons and Fehrer⁵ have also failed to record the O-H frequency in the phosphoric, phosphorus and hypophosphorus acids and they have concluded that these acids exist in the true acid form and not as pseudo-acids⁶ possessing hydroxyl groups.

The present investigation* was undertaken in order to decide whether the hydroxyl frequency exists or not in inorganic acids. The results have also been discussed in relation to the so-called 'hydrogen bond' in these compounds.

2. Experimental.

Since the frequency due to the O-H group falls almost in the same region as the Raman bands of water, it is important that for the purpose of this investigation, the substances examined should be in the anhydrous condition. Among the substances studied, sulphuric acid was in 100 per cent. liquid state, free from water and thrice distilled in vacuum. The crystals of iodic, selenious and telluric acids and sodium dihydrogen phosphate and potassium bisulphate were dried in a desiccator and examined in an air-tight tube. The crystals were investigated by the method of complementary filters devised by Ananthakrishnan,⁷ which yields a remarkably clear region between 4358 and 4916 Å., where these bands appear. In the case of liquid sulphuric acid only one filter was used in the path of the incident light to cut off the 4358 radiations of the source. The times of exposure ranged from 3 to 6 days.

3. Results.

All compounds studied have yielded a broad and weak band at about 2900 to 3400 cm.^{-1} . The frequency shifts and the breadth of this band are given in Table I. The other vibration frequencies in these substances† are not included, since they do not come into consideration in the present investigation. The last column in the table gives the difference between the frequency shift of the centre of the band and the free hydroxyl frequency, 3608 cm.^{-1} , as observed in potassium hydroxide.

⁵ Simons, A., and Fehrer, F., *Zeit. f. Anorg. u. Allg. Chem.*, 1936, 230, 289.

⁶ Hantzsch, *Ber.*, 1925, 58, 941.

* A preliminary note on the results of this investigation was published in *Nature*, 1937, 140, 151.

⁷ Ananthakrishnan, R., *Proc. Ind. Acad. Sci.*, (A), 1937, 5, 76.

† Solid selenious acid has yielded a new weak line at 2217 cm.^{-1} , which has to be attributed to Se-H oscillations. (*Vide* C. S. Venkateswaran, *Proc. Ind. Acad. Sci.*, (A), 1936, 3, 533.)

TABLE I.
Exciting line 4046.5 Å.

Substance	Raman band of O-H in cm. ⁻¹			Deviation from normal
	Beginning	Middle	End	
H ₂ SO ₄ 100% liquid	2794	2985	3172	623
HIO ₃ crystals	2834	2979	3125	629
H ₂ SeO ₃ „	2973	3057	3141	551
H ₆ TeO ₆ * „	2985	3121	3257	487
NaH ₂ PO ₄ „		3460 ±20		148
KHSO ₄ „	2750	to	3800	

* Telluric acid solution has yielded three vibration lines with frequency shifts 647 (10), 624 (1) and 357 (4), of which 647 is highly polarised and the other two are depolarised.

The following characteristic features of the bands may be noted:—
(1) The O-H frequency in these acids and acid salts is represented by a band which is weak, broad and diffuse as compared with the other vibration frequencies in their spectra. (2) The magnitude of the frequency shift of this band is considerably lower than the O-H frequency in potassium hydroxide. It is also distinctly lower than the well-known bands of water at 3205, 3420 and 3580 cm.⁻¹, and therefore there is no possibility of confusing with the latter. (3) There is a progressive fall in the frequency shift and a diminution of the intensity and increase in diffuseness of the band as the strength of the acid increases. (4) In the case of sulphuric acid the band appears to be resolved into two components. (5) The O-H band in NaH₂PO₄ is weak, but comparatively narrow and has a greater shift. In KHSO₄ the band appears only as a weak, diffuse darkening extending from 2750 to 3800 cm.⁻¹

4. Discussion of Results.

1. *In relation to electrolytic dissociation and molecular structure.*—According to Martin and his collaborators,⁴ if the oxyacids exist in the unionised state in the concentrated aqueous solutions, the dissociation of the molecules takes place about the O-H bond and hence the obvious method of investigation of the degree of dissociation by the Raman effect is to follow the changes in the intensity of the band due to the hydroxyl group. In a second

communication⁸ they have also arrived at the result that the frequency characteristic of the O-H group in compounds containing that group has a fairly constant value of about 3500 cm.⁻¹ Both of these conclusions require modification. The results given in Table I show that in all the acids studied, the weak and diffuse band appearing at about 3000 cm.⁻¹ could be assigned only to the hydroxyl group in them. A similar band reported in the literature for a number of other acids is given in Table II. While the existence

TABLE II.

Acid	Frequency shift in cm. ⁻¹			Deviation from normal	References
	Beginning	Middle	End		
HNO ₃		3070		538	W. H. M.
H ₃ PO ₄	2700	3360	3700	248	Méd.
H ₃ AsO ₄	3060	3470	3670	138	F. and M.
H ₃ BO ₃	3172	3256		352	R. A.
HCOOH		3350		258	L. B.

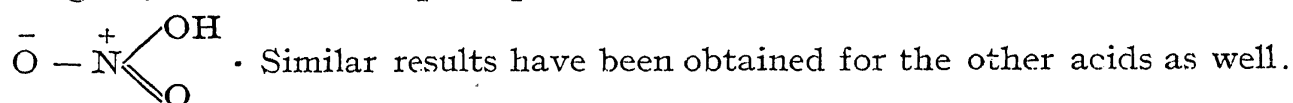
W. H. M. = Martin, W. H., and others, *loc. cit.*; Méd = Médard, *Compt. Rend.*, 1934, 198, 1407; F. and M. = Fehrer and Morgenstern, *loc. cit.*; R. A. = Ananthakrishnan, R., *Proc. Ind. Acad. Sci.*, (A), 1937, 5, 200; and L. B. = *Landolt-Bornstein Tabellen*, Weiler.

of this band in all these acids proves the presence of the hydroxyl group, their low intensity does not permit of even qualitative measurements of the study of progressive dissociation with increasing dilution. The extreme feebleness of these bands cannot be explained as due to the presence of only a few undissociated molecules in the pure state, but has to be attributed to the same cause as the diffuseness and the lowering of the frequency of these bands.

From the presence of the OH band in the acids cited in Tables I and II, we are led to conclude that they exist in the form of pseudo-acids. This conclusion is further justified by the fact that in concentrated solutions of these acids, a greater number of Raman lines has been recorded than is to be expected if the molecules were in the true acid form. Thus for the nitric acid the true acid form, (HNO₃), should yield only three lines similar to the NO₃ ion, but in fact, six lines have been recorded which could be

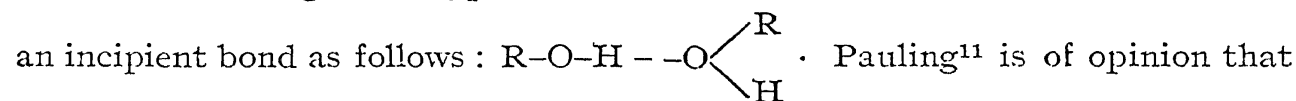
⁸ Bernstein, H. J., Romans, R. G., Howden, O. H., and Martin, W. H., *Trans. Roy. Soc.*, Canada, 1936, 49, 37.

assigned, with the help of polarisation data,⁹ to a pyramidal molecule



The failure to record the O-H band in the acids of phosphorus by Simons and others is probably due to the heavy background present in their spectra. The results of Fehér and Morgenstern with arsenic acid, however, which is homologous to phosphoric acid in all its properties, are in agreement with the pseudo-form of the acid molecule.

2. *In relation to the 'hydrogen bond'.*—The presence of the band characteristic of the O-H group in the acids and the acid salts referred to in Tables I and II is also significant from the point of view of the so-called hydrogen bond put forward by Latimer and Rodebush.¹⁰ By hydrogen bond is meant a chemical linkage in which a hydrogen atom usually belonging to a hydroxyl or amino group causes an intermolecular association of two or more molecules or an intramolecular binding (chelate ring) in a single molecule whenever the configuration is favourable. Thus, the association of molecules of the general type ROH is explained as due to the formation of



whenever a hydrogen bond is formed during association or chelation, the hydrogen involved in the linkage no longer remains attached to a particular oxygen atom, but is in a state in which it is equally shared by the two oxygen or electronegative atoms. In such cases, the electronegative atoms are brought nearer to each other. The hydrogen atom will be in a state of resonance between the two and no definite O-H bond will be established.

The experimental evidence in support of the existence of the hydrogen bond in hydroxy compounds is furnished by the crystal structure data which indicate that in such compounds the oxygen-oxygen distance has an extremely low value of 2.55 Å., while double the radius of the ion O⁻ is 2.70 Å. and of the neutral oxygen is 3.9 Å. Hilbert, Wulf, Hendricks and Liddel¹² have shown that the hydroxyl group involved in a hydrogen bond does not yield the infra-red absorption characteristic of the group and suggested that the absence of this band may be taken as a criterion for the

⁹ Venkateswaran, C. S., *Proc. Ind. Acad. Sci., (A)*, 1936, 4, 174.

¹⁰ Latimer, W. M., and Rodebush, W. H., *J. Amer. Chem. Soc.*, 1920, 42, 1419.

¹¹ Pauling, L., *ibid.*, 1936, 58, 94.

¹² Hilbert, G. E., Wulf, O. R., Hendricks, S. R., and Liddel, U., *Nature*, 1935, 135, 147.

formation of the hydrogen bond. Recent investigations in the infra-red absorption by Errera and Mollet,¹³ Buswell, Dietz and Rodebush,¹⁴ Fox and Martin,¹⁵ and Badger and Bauer¹⁶ have shown, however, that in a number of cases in which the hydroxyl group is known to be linked by a hydrogen bond, the narrow band at 2.769μ characteristic of the free O-H does not disappear completely as Wulf and his co-workers thought, but appears as a broad, intense band at a longer wave-length of about 3μ . The change in the wave-length is attributed by them to a weakening of the O-H bond. These investigations in the infra-red are mostly confined to organic compounds and the simultaneous presence of certain C-H frequencies in the above region is a great handicap for the exact determination of the position of the shifted band.

All the substances included in the present investigation possess one or more hydroxyl groups and are known to contain the hydrogen bond. They are also free from C-H group and any shift in the region of 3000 cm.^{-1} has to be assigned only to O-H oscillations. The results given in Table I give for the first time the characteristic features of the Raman band of the hydroxyl group involved in a hydrogen bond. The following conclusions may be made :—

1. There is a definite Raman spectrum for the hydroxyl groups in compounds which possess hydrogen bond.
2. The frequency of this band is considerably lower than the free hydroxyl frequency. The magnitude of lowering is a maximum in sulphuric acid and gets smaller as the strength of the acid diminishes. In dihydrogen sodium phosphate the frequency shift is of the same order as in alcohols.
3. The breadth of the band is greater the more the lowering in the frequency shifts. The diffuseness of these bands is in agreement with the results of the infra-red absorption.
4. Though the band characteristic of the hydrogen bond is intense in the infra-red absorption, it is very weak in Raman scattering. It is not possible from the present investigation to obtain any idea about the relative intensities of this band in different compounds.

An approximate estimate of the change in the energy caused in the O-H linkage due to the formation of the hydrogen bond is made by Fox and Martin and they have shown that in phenol and alcohols in which the

¹³ Errera, J., and Mollet, P., *Nature*, 1936, 138, 882.

¹⁴ Buswell, A. M., Dietz, V., and Rodebush, W. H., *J. Chem. Phys.*, 1937, 5, 501.

¹⁵ Fox, J. J., and Martin, A. E., *Proc. Roy. Soc.*, (A), 1937, 162, 419.

¹⁶ Badger, R. M., and Bauer, S. H., *J. Chem. Phys.*, 1937, 5, 839 and 852.

band appears at a frequency of 150 to 300 cm.^{-1} lower than the free O-H band, the energy involved will be between 3000 and 6000 cal./mol. Following their method of calculation, this change in the energy is a maximum in sulphuric acid and will be about 12,500 cal./mol. This is slightly less than $\frac{1}{8}$ of the dissociation energy of the normal O-H bond; but compared to the changes of energy in associated alcohols it is considerable and hence we have to conclude that the hydrogen bond is very strong in it.

TABLE III.

Substance	Frequencies in cm.^{-1}			Substance	Frequencies in cm.^{-1}
H-O-H vapour	3646 st	3654 st		Ba(OH) ₂	3417 vw
„ liquid	3205 m	3420 st	3580 w	CH ₃ OH	3430 (400 cm.^{-1}) b broad
„ solid 0° C.	3200 st	3321 m, b		C ₂ H ₅ OH	3240 3359 m, b, st, b
„ „ -190° C.	3090 st	3135 w		C ₃ H ₇ OH	3400 b
H ₂ O ₂	3395 m, b			C ₄ H ₉ OH	3400 b
NaOH	3630 st			glycol	3250 to 3550
KOH	3608 st			glycerin	3450
Sr(OH) ₂	3484 w			Phenol	3500

Note *st* = strong, *m* = medium intensity, *w* = weak, *vw* = very weak and *b* = broad.

In Table III the available data¹⁷ on the O-H Raman frequency in a few hydroxides and alcohols are recorded. It may be seen that while the alkali hydroxides give the maximum frequency shift of about 3600 cm.^{-1} , there is a distinct lowering of frequency in the other compounds. The diminution of frequency is, however, much less than in the case of the strong acids given in Tables I and II. As in acids, this lowering of the O-H frequency in these cases has to be attributed to the formation of inter- or intra-molecular linkage involving the formation of a hydrogen bond. On the basis of this conception, we have to postulate that the water molecules

¹⁷ For references see *Landolt-Bornstein Tabellen*, Weiler.

are unassociated in the vapour state ; but in the liquid and solid states they are associated through hydrogen bonds, the strength of this bond increasing with decrease of temperature.

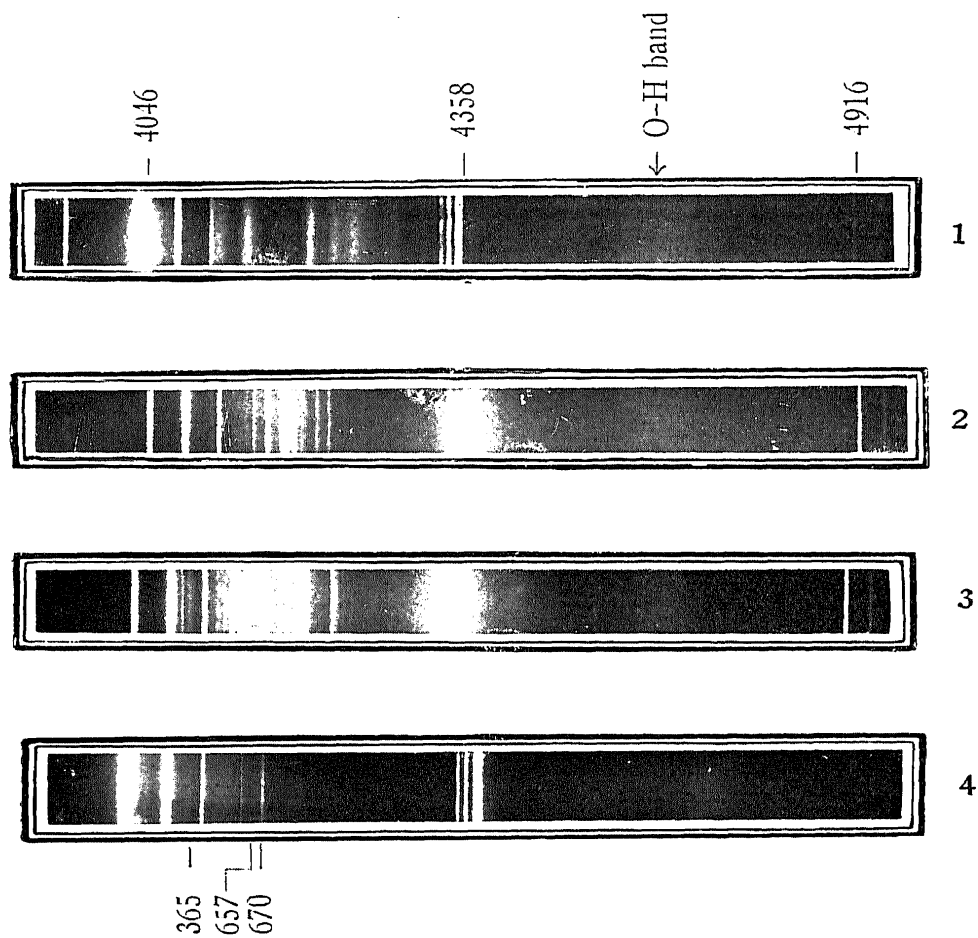
According to Bernal and Megaw,¹⁸ a distinction should be made between hydrogen bond and hydroxyl bond. In the hydrogen bond, the hydrogen atom is in a state of oscillation between two oxygen atoms and there is no definite OH group and the O-O distance is reduced to 2.55 Å. In the hydroxyl bond, the hydrogen atom remains attached to one oxygen atom, but is at the same time linked to another electronegative atom, which tends to weaken the O-H bond and the O-O distance is greater than 2.7 Å. It appears to the author that this distinction between the two kinds of bonds is artificial. If the results in Tables I, II and III are taken together, it will be seen that the change in the hydroxyl frequency is graded and in no case has it completely disappeared. We have to conclude from this that an incipient chemical linkage called 'hydrogen bond' is formed in all these compounds causing association between two or more molecules or chelation in single molecule, the strength of the linkage alone varying from compound to compound. The hydroxyl group preserves its identity in all cases ; but its bond strength is diminished in a manner proportionate to the strength of the hydrogen bond. The diffuseness and the extreme weakness of the Raman band due to the hydrogen bond, however, requires explanation.

In conclusion, the author wishes to express his respectful thanks to Sir C. V. Raman for his kind interest in the work.

Summary.

The Raman spectra of sulphuric, iodic, selenious and telluric acids and sodium dihydrogen phosphate and potassium bisulphate have been obtained under long exposure and using complementary filters. In every case, a band characteristic of the O-H group has been recorded. The band is weak and diffuse and is shifted to a frequency considerably lower than that due to free hydroxyl group. The results are discussed in relation to electrolytic dissociation and molecular structure of these compounds. From the nature of the spectra, the characteristic features of the Raman band due to the so-called hydrogen bond are deduced. Some new Raman frequencies in selenious and telluric acids are indicated in the paper.

¹⁸ Bernal, J. D., and Megaw, H. D., *Proc. Roy. Soc., (A)*, 1935, 151, 384.



The Raman Spectra.

1. H_2SO_4 . 2. HIO_3 . 3. H_2SeO_3 . 4. H_6TeO_6 .