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Vibration Spectra and Molecular Structure

I. General Remarks and a Study of the Spectrum of the OH Group

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(Received August 5, 1936)

A brief survey is given of the ideas underlying the interpretation of molecular vibration spectra in connection with molecular structure problems. This is followed by a discussion of the reasons for the appearance or nonappearance in the spectrum of the characteristic frequency at 3400 cm^{-1} for various molecules containing the OH group. In certain alcohols and glycols this frequency has not been reported in the Raman effect, but it is concluded that this must be due to experimental difficulties. In the carboxylic acids, on the other hand, as well as in certain aromatic compounds containing OH, the characteristic frequency is definitely absent from both the Raman and infrared spectra, and the role of the hydrogen bond in association and chelation is discussed in connection with these cases.

INTRODUCTION

STUDY of molecular structure by means of infrared and Raman spectra has progressed in two directions. One attack may be said to derive from the highly developed subject of diatomic molecular spectroscopy. Here triatomic molecules and the simpler molecules of four, five and six atoms are studied with high resolution and carefully analyzed in terms of accurate solutions of the complicated vibration problems involved. Progress in this direction is necessarily slow and beset with many difficulties.

Another attack corresponds to the one which has received attention for many years—the semi-quantitative, half-empirical correlation of observed frequencies to individual valence bonds in the molecule. In spite of the vast amount of work that has been put on this side of the subject we believe that there is still a great deal to be learned about molecular structure by a critical discussion of the data in terms of these less precise methods. Not only can many questions of molecular structure be answered in this way now, but a careful study of the empirical material from this standpoint will be a necessary preliminary to the extension of precision methods to complicated molecules. Therefore it is our intention in the series of papers of which this is the first, to make a careful survey of the empirical material in terms of the simpler methods of interpretation.

This paper includes a survey of the general

ideas used and a discussion of factors affecting the appearance of the band due to the hydroxyl group in various compounds.

Valence bond frequencies

A well-known fact of infrared spectroscopy and of its lusty nephew, Raman spectroscopy, is that certain frequencies can be correlated closely with the occurrence in the molecule of certain valence bonds. Curiously enough such correlations are often more constant and uniform in complicated molecules, the notable departures occurring in the lowest members of homologous series. This is connected with the fact that symmetry restrictions usually affect the simpler molecules while in more complicated structures the symmetry elements are lost. Also, in a series of complex molecules the environment of a given bond is more likely to be constant.

If the situation were so simple that there would always be associated a vibration frequency with each type of bond in the molecule, then obviously the molecular vibration method of analysis would provide a very powerful means of investigating the structures of molecules. The situation is in fact almost that simple and a large part of the spectrum in the fundamental vibration region is understandable at a glance. In a recent paper by one of us¹ there is given a brief survey of the type of problem to which these methods are applicable, and of the mode of attack used in some cases. Suffice it to say that important informa-

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** National Research Fellow.

¹ R. B. Barnes, *Rev. Sci. Inst.* **7**, 265 (1936).

tion has already been obtained in the fields of deuteriochemistry, polymerization, isomerism, chelation, and many others and that the possible extensions in these and other fields appear to be almost unlimited. In the present paper we wish to point out that exceptions to the principle of constant bond frequencies frequently occur, and that from these exceptions information is obtained which is just as valuable as that obtained from the regularities. When such exceptions occur it is often possible to give a simple dynamical explanation in terms of the vibration forms of the molecule. If such an explanation is not possible it can frequently be shown that the classical structural formula of the molecule under investigation is not entirely correct.

As regards the dynamical effects mentioned above, it should be pointed out that it is the bond force constant and not the position of the infrared absorption or Raman frequency that is characteristic of the specific bond. Therefore a knowledge of these bond force constants is essential if the effects on the positions of the molecular frequencies caused by such phenomena as the interaction between two neighboring similar bonds is to be correctly explained. For this reason frequent reference will be made in what follows to the values of these constants and to the methods used in their calculation.

Following the ideas of Mecke, Dennison, Sutherland and others²⁻⁴ we suppose the principal forces involved are those of a valence force system, namely forces between those atoms which are chemically bonded, obeying Hooke's law for small displacements from equilibrium, and a system of torques tending to preserve the bond angles at the tetrahedral value for carbon and at the appropriate other angles for other polyvalent atoms. In the more accurate analyses other terms are inserted to represent interaction forces between different valence bonds but their effects are usually small.

The next point to make is that accurate analysis of simpler cases has shown the forces preserving valence angles to be much weaker than those available for preserving bond dis-

tances. This fact together with the fact that "straight-chain" compounds are actually zigzag in form tends to reduce the amount of dynamical interaction between different valence bond oscillations, as was pointed out by Bartholomé and Teller⁵ and recently by Bauermeister and Weizel.⁶ Because of the weakness of the directed valence forces those frequencies in which angles vary are generally lower in value than the valence oscillations, being generally less than 1000 cm⁻¹. Also as a result of this weakness the deformation frequencies are affected more strongly by neighboring atoms or groups and do not show such simple empirical regularities as the valence oscillations. They will, therefore, receive almost no consideration in what follows.

To the approximation that Hooke's law forces are obeyed, every theoretical formula relating a vibration frequency to the force constants and masses in a molecule will have a dimensional similarity with that for the simple harmonic oscillator,

$$\bar{\nu} = (2\pi c)^{-1}(k/m)^{1/2}. \quad (1)$$

Here $\bar{\nu}$ is the frequency in cm⁻¹, m is the mass and k is the force constant in the equation connecting potential energy, V and displacement x from the equilibrium position,

$$V = \frac{1}{2} kx^2. \quad (2)$$

It is convenient to standardize the units, once and for all. All known values of the force constant are of the order of 10⁵ dyne/cm so we shall adopt this as a convenient unit for k . We have:

$$\begin{aligned} 10^5 \text{ dyne/cm} &= 10^5 \text{ erg/cm}^2 = 6.284 \text{ eV/\AA}^2 \\ &= 509.5 \text{ cm}^{-1}/(10^{-9} \text{ cm})^2 \\ &= 1.449 \text{ (cal/mole)}/(10^{-9} \text{ cm})^2, \end{aligned} \quad (3)$$

which enables conversions of k to other energy and length units to be readily made. For the masses it is convenient to use atomic weights on the oxygen = 16 scale. Using Birge's values for the universal constants the formula that is the dimensional model for all normal modes solutions of vibration problems becomes

$$\bar{\nu} = 1307 (k/m)^{1/2}. \quad (1')$$

We turn now to a rapid survey of the funda-

² R. Mecke, *Zeits. f. physik. Chemie* **B16**, 409, 421; **B17**, 1 (1932).

³ D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

⁴ Sutherland and Dennison, *Proc. Roy. Soc.* **A148**, 250 (1935).

⁵ Bartholomé and Teller, *Zeits. f. physik. Chemie* **B19**, 366 (1932).

⁶ Bauermeister and Weizel, *Physik. Zeits.* **37**, 169 (1936).

mental frequencies and force constants characteristic of bonds of the type commonly occurring in organic molecules.

Single bonds with hydrogen: CH, OH, NH, SH

Nearly every molecule considered contains one or more CH bonds. All such show infrared absorption and Raman lines between 2600 and 3050 cm^{-1} , the strongest frequencies in aliphatic molecules being generally close to 2900. In aromatic molecules the frequency is generally higher being near 3050 as a rule. The simplest view of the matter is to suppose the CH bonds capable of vibration pretty much as independent units in spite of their being part of the larger structure. To that approximation the frequency is given by (1).

With increasing complexity of structure the number of frequencies attributable to CH increases. Here, however, the emphasis is on the comparatively narrow range of these frequencies. The frequency 2918 in methane corresponds to symmetric contraction-expansion of the tetrahedron: here the carbon stands still and the four hydrogen atoms move with alteration of the four bond distances. The frequency may be calculated from (1') with $m=1$, and k the constant for the CH bond. This yields a value of $k=5.00$ which agrees well with the value 5.02 obtained by Bonner⁷ from a detailed analysis for ethylene. For further comparison we note that the frequency in the normal electronic state of CH in the diatomic band system is 2859, which together with the reduced mass value 0.924 gives 4.44 for k . Provisionally we postulate that k has the value 5.00 for all organic CH bonds.

Characteristic of all compounds containing the OH group is a frequency close to 3400. Since this group has many interesting special properties and since there is a good deal of confusion about it in the literature it is dealt with in detail in the latter part of this paper. In diatomic OH from electronic bands, the normal state frequency is 3735 corresponding to $k=7.72$ while in H_2O vapor the two normal modes which are essentially valence oscillations are 3600 and 3756, and the force constant for OH found in Bonner's⁸ analysis of the water spectrum is 8.233. The value ob-

tained from 3400 assuming the H to be vibrating against a large mass (reduced mass = 1) is $k=6.8$.

Frequencies characteristic of the NH bond are not greatly different from those for OH, being in the region around 3300. Here the force constant from the diatomic frequency is 5.22 while that calculated from the frequency 3320 using for the reduced mass $\mu=1$ is 6.4.

These three commonest types of bonds involving hydrogen have therefore frequencies in the range from 2800 to 3400 and may give rise to some overlapping in infrared studies with low dispersion, as with a single prism rocksalt instrument. Nevertheless it is often possible to distinguish between the bands due to these bonds as will appear later.

Characteristic of SH is a remarkably constant frequency which stays between 2570 and 2580 in the mercaptans. This is a convenient location as it happens that there are usually no other bands in this immediate neighborhood. This frequency corresponds to the much weaker force constant $k=3.85$.

Single bonds: C—C, C—O, C—N

After CH, the CC linkage occurs most frequently in organic chemistry. For the single bond CC linkage the general range of frequencies is 800 to 1150. Here there is a tendency to develop a fairly open structure of increasing complexity with growing length of carbon chain. This interaction splitting continues as the length of the chain increases, and leads to the often observed differences between the spectra of the first and higher members of homologous series. This effect has been treated recently by Bauermeister and Weizel.⁶

In ethane, for example, we find a single CC frequency at 993, whereas in propane we find two frequencies characteristic of this bond, one at 867 and the other at 1055. This splitting is an example of the type of dynamical interaction mentioned above, resulting from the presence in the molecule of adjacent similar bonds. Further examples are found in the spectra of the C—O—C and the C=C=C groups

At this point it is perhaps timely to say a few words concerning a useful approximate method of force constant calculation introduced by Mecke,² and used with considerable success by him and by

⁷ L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

⁸ L. G. Bonner, Phys. Rev. **46**, 458 (1934).

Sutherland and Dennison.⁴ Since the hydrogen atoms, which are found on practically all molecules investigated to date, are very light, and their vibration frequencies as have been shown are high compared with those of neighboring groups of heavier atoms, it is frequently possible to neglect the effect of these hydrogens and to treat the groups containing hydrogen as rigid bodies. To this approximation, ethane would be treated as a diatomic molecule, each body being of mass 15, while propane would be triatomic, with two mass 15 bodies and one of mass 14. The applications and limitations of this rigid group approximation will be illustrated for a few cases in what follows, and will be taken up in considerable detail in later papers of this series. As an example of such a simplified calculation, ethane with a reduced mass of 7.5 yields a force constant $k = 4.32$, which is an entirely reasonable value.

The single bond CO frequency is not always recognizable since it is so close to the single bond CC frequency. However, in methyl alcohol the frequency 1030 is readily associated with this vibration. Regarding it as a vibration of OH against CH₃ this gives $k = 4.96$ for the CO force constant.

Since what has been said above illustrates well the behavior of bond frequencies and the approximate constancy of the force constants deduced therefrom, we feel it to be unnecessary to discuss further cases in detail. At this point we shall point out simply the ranges of the frequencies and force constants associated with some of the remaining principal bond types. For a detailed compilation of the frequency values the reader is referred to standard works, such as those of Schaeffer and Matossi,⁹ Kohlrausch¹⁰ and Hibben.¹¹

To repeat, for purposes of comparison, the single bond values given above, we find that, for single bonds between light atoms the frequencies all lie in the range 800–1150 cm⁻¹ and the force constants between 4 and 5 (in units of 10⁵ dynes/cm). Double bond frequencies are generally between 1500 and 1800 corresponding to a force constant in the neighborhood of 10–12.

The triple bond, again, is still higher, ranging from 1900–2300, with a force constant range of 15–20. In the methyl halides frequencies probably to be associated with the C–Cl, C–Br, and C–I bonds are found at 710, 600, and 530, respectively. It must be emphasized that these values apply principally to the aliphatic or open chain compounds and may differ appreciably from the frequencies for the same combinations existing in ring structures.

It is hoped that with this brief introduction we have made clear the empirical background underlying these studies and have outlined the aims, methods and terminology of these papers.

THE SPECTRUM OF THE OH GROUP

Since the assumptions implied above are that any molecule containing an OH group will have a frequency in the neighborhood of 3400 cm⁻¹ and since many molecules which are known, by chemical evidence, to have such a group do not exhibit this frequency, one must look for an explanation of this apparent anomaly. In what follows we propose to point out some of the principal exceptions to this rule of constant bond frequencies and to draw attention to some of the factors that may lead to the disappearance of this frequency.

Raman effect

Careful study of the original literature and of the reviews mentioned above reveals the remarkable fact that throughout the period of development through which the Raman effect has passed since its discovery in 1928 the overwhelming majority of observers failed consistently to record frequencies in the 3400 region. In view of the fact that the strong band which occurs in the infrared spectra of all alcohols at about 2.9 μ (3400 cm⁻¹) has, since the days of Julius and Aschkinass been identified with the internal vibration of the OH group, it is extremely surprising that this Raman frequency should continue to be conspicuous by its absence. On page 17 of his review, Hibben states, with regard to the 3400 shift, "Unfortunately . . . this can only be detected in less than half the alcohols studied." On page 20 one sees that neither propylene glycol, glycerol nor glucose shows an OH frequency at 3400, if the list of frequencies reported is to be taken as complete.

⁹ Schaeffer and Matossi, *Das Ultrarote Spektrum*.

¹⁰ Kohlrausch, *Der Smekal Raman Effekt*.

¹¹ J. H. Hibben, *Chem. Rev.* **18**, 1 (1936).

Wood and Collins¹² recently reported Raman measurements upon a beautifully complete series of eleven normal alcohols but failed to record any frequency higher than 3000. Venkateswaran and Bhagavantam¹³ presented an extensive table of frequencies observed for alcohols; none, however, higher than 3000 cm^{-1} . In a footnote they remarked that "The Raman spectrum of methyl alcohol shows, besides the lines given, . . . a prominent broad band corresponding to a shift of about 3μ" The implication is that the remaining alcohols did not contain even this broad band. So it is with numerous other observers and in the cases of many other compounds containing OH. In view of the fact that all of the compounds herein mentioned do exhibit strong OH absorption in the infrared, as shown in part in curves 1-5 of the figure, and since most of them are reasonably complex molecules so that the possibility of the corresponding Raman frequencies being forbidden by selection rules based on symmetry is very small, the absence of these frequencies is puzzling. Recent Raman measurements in this laboratory have indicated the presence of the weak broad band at about 3400 cm^{-1} characteristic of the OH group, in two of the compounds mentioned above, namely propylene glycol and glycerol. As a result it is clear that caution must be used in basing analyses of the type mentioned in the introduction solely on the results of Raman measurements. The authors have found that a good general principle to be applied in the interpretation of Raman results is that, although the appearance of a line is definite, the nonappearance may be due to any one of a number of factors and does not necessarily indicate that the frequency is absent in the molecule.

Infrared

As already mentioned, all the alcohols heretofore measured have shown a strong OH absorption in the infrared, and, in fact, practically all compounds containing OH exhibit this band. There are, however, a few cases in which this absorption is definitely absent, and it is to these that we shall turn our attention.

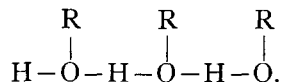
¹² Wood and Collins, *Phys. Rev.* **42**, 386 (1932).

¹³ Venkateswaran and Bhagavantam, *Ind. J. Phys.* **5**, 129 (1930).

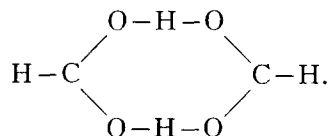
Molecules containing the carboxyl group

Sappenfield,¹⁴ Eichmann,¹⁵ Roth,¹⁶ and Errera and Mollet¹⁷ have all reported on infrared absorption of the fatty acid series, and are all in agreement that the overtones of the 3400 frequency are missing in the lower members. In addition measurements in this laboratory on formic, acetic, propionic and valeric acids in the fundamental region show that this frequency is missing for the lower members and appears only very weakly for some of the higher members of the series. This effect is exemplified by curves 6 and 7 of the figure.

The fatty acids are in general highly associated, some fifty percent of the molecules of the lower members existing as dimers even in the vapor state at an elevated temperature, according to Drucker and Ullmann.¹⁸ This gives us the explanation for the disappearance of this band. According to Sidgwick,¹⁹ this association takes place through the OH group of each interacting molecule, as given by the structural formula



Pauling and Brockway,²⁰ however, have shown by electron diffraction experiments that the dimer of formic acid has a ring structure of the form



In either case, since a hydrogen bond is formed between the oxygen atoms of two separate molecules, it seems clear that the bonding between H and O must be different from that in normal OH, with a corresponding effect on the vibration frequency. In fact, Pauling and Brockway showed that the O—O distance in the formic acid dimer is 2.66Å, indicating that the O—H distance is perhaps 1.33Å, rather than the normal 0.96Å.

¹⁴ J. W. Sappenfield, *Phys. Rev.* **33**, 37 (1929).

¹⁵ O. Eichmann, *Zeits. f. Physik* **82**, 461 (1933).

¹⁶ A. Roth, *Zeits. f. Physik* **87**, 192 (1933).

¹⁷ J. Errera and P. Mollet, *J. de physique* **7**, 281 (1935).

¹⁸ Drucker and Ullman *Zeits. f. physik. Chemie* **74**, 604 (1910).

¹⁹ Sidgwick, *The Electronic Theory of Valence* (Oxford, 1929).

²⁰ L. Pauling and L. Brockway, *Proc. Nat. Acad. Sci.* **20**, 336 (1934).

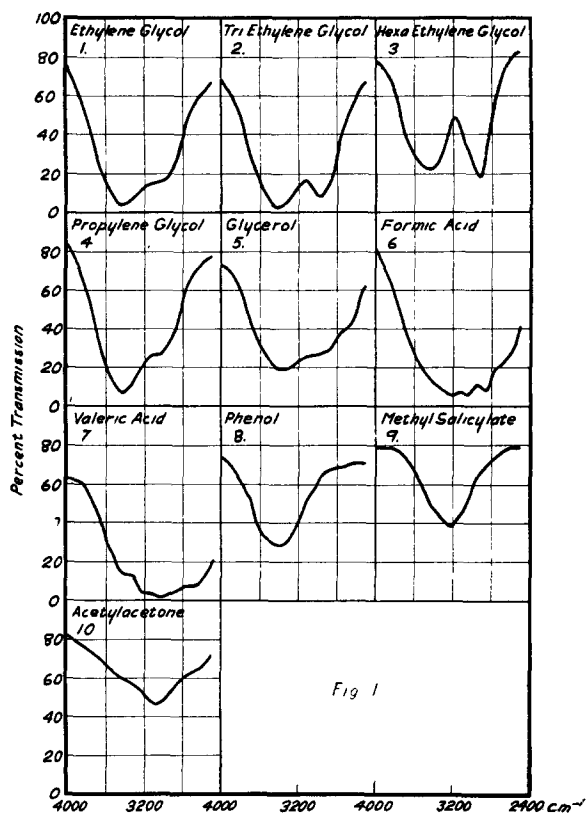


FIG. 1. These infrared transmission curves cover, for several compounds containing the hydroxyl group, the regions of the fundamental OH and CH absorptions at about 3400 and 3000 cm^{-1} , respectively. The absence of the OH absorption is to be noted in formic acid, methyl salicylate and acetylacetone, curves 6, 9 and 10.

Association through linkage of the OH appears to a certain extent in most hydroxyl containing molecules, and the relative intensity of the 3400 absorption region provides an indication as to the extent to which this has taken place. Even the alcohols, which were cited above as showing the OH frequency in the infrared, are known to be slightly associated. Kinsey and Ellis²¹ found that the characteristic band, for the case of methyl alcohol, was shifted slightly, sharpened, and increased in intensity by passing from the liquid to a solution in CCl_4 . Dilution with a solvent tends, of course, to diminish association, and Kinsey and Ellis found that the absorption in solution bore a close resemblance to that of the vapor, which is almost certainly unassociated. As might be expected, an increase in temperature also has a tendency to decrease the degree of

²¹ E. L. Kinsey and J. W. Ellis, *Phys. Rev.* **49**, 105 (1936).

association, as was shown by experiments of Bloch and Errera.²²

Molecular association is affected by the weight and volume of the interacting molecules, as illustrated by curves 6 and 7. In formic acid the OH absorption is completely lacking, while in valeric there does appear a slight trace of absorption in this region. This same effect has been found by Errera and Mollet,¹⁷ who investigated a series of acids, including caproic, in the overtone region.

Chelated compounds

It has been shown that in a number of compounds, principally aromatic compounds containing an OH in the *ortho* position to a $\text{C}=\text{O}$ or $\text{N}=\text{O}$, the possibility exists of forming a ring. This ring, usually six membered, is closed by a hydrogen bond, again involving the hydrogen of the OH group. Both Sidgwick and Errera and Mollet present much evidence of a chemical and physical nature justifying the ring structure for methyl salicylate, salicylaldehyde and many other similar compounds. The final proof seems to be supplied by the fact that none of these compounds exhibit any OH absorption, as was shown by Errera and Mollet and by Hilbert, Wulf, Hendricks and Liddel²³ by measurements in the overtone region. Curves 8 and 9, taken in this laboratory, show how, in the fundamental region, the strong OH band of phenol is completely wiped out when the $\text{C}=\text{O}$ is placed in the *ortho* position to it in methyl salicylate. Acetylacetone, which is known from other evidence to exist almost entirely in the enol form, is also capable of forming a chelate ring, as is shown by the absence of the 3400 band in curve 10.

In the case of these compounds, as also for the fatty acids, it is interesting to speculate as to the fate of this OH absorption band. Certainly, even though the frequency is greatly affected, there must still be some vibration characteristic of the motion of H against O, though it has not yet been located. It seems reasonably certain that the strength of such a hydrogen bond is only a small fraction of that of the normal OH bond. That is to say, the dissociation energy of the $\text{O}-\text{H}-\text{O}$ link formed in associated or chelated compounds

²² B. Bloch and J. Errera, *J. de physique* **6**, 154 (1935).

²³ Hilbert, Wulf, Hendricks and Liddel, *Nature* **135**, 147 (1935).

is of the same order of magnitude as that of an ordinary OH. In formic acid Pauling and Brockway found, however, that the distance between two oxygen atoms bound by a hydrogen bond was about 2.67Å, which agrees well with previous crystal structure values, and with distances calculated by Errera and Mollet from known angles and distances alone. If, then, the H atom remains at approximately the normal distance of 0.96Å from the oxygen to which it was originally bonded it will be 1.71Å from the other. It is known that interatomic forces decrease very rapidly with distance so the vibration in this case would be essentially H against one O and the energy consideration given above would indicate that the frequency would be almost unchanged. Since this is obviously not so, let us turn to the perhaps more reasonable case of the hydrogen atom midway between the two oxygens, with the force so distributed that each OH bond is the same. Assuming that the force constant varies with distance in the inverse cube fashion suggested by Badger²⁴ it is possible to calculate the OH vibration frequency for this case. Assuming further

²⁴ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934).

that the oxygen atoms are stationary and that the equilibrium O—H distance is 1.33Å we find, that the 3400 cm⁻¹ frequency shifts to nearer 2400. However, it is not necessary that the H lie on the O—O line and the O—H separation may be larger than that used above. Below are given frequency values corresponding to several O—H separations, taking the O—O distance constant at 2.67Å.

r	1.33	1.40	1.50	1.60	1.70
$\bar{\nu}$	2390	2050	1680	1390	1170.

In a recent paper Gillette and Sherman²⁵ seem to favor a structure for the formic acid dimer in which the hydrogen atom, while located on the line of centers of the oxygen atoms, is neither in the center nor at the normal O—H distance from one. This would lead to a vibration frequency between the above 2400 and 3400 cm⁻¹. It would appear from this that almost any value of the OH frequency in compounds of this type would be reasonable, and it is unfortunate that as yet no spectrum has been analyzed carefully enough to permit of its identification.

²⁵ R. H. Gillette and A. Sherman, *J. Am. Chem. Soc.* **58**, 1135 (1936).

The Relative Atomic Weight of Oxygen in Water and in Air

II. A Note on the Relative Atomic Weight of Oxygen in Fresh Water, Salt Water and Atmospheric Water Vapor

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(Received September 12, 1936)

Purified Lake Michigan water appears to be nearly exactly intermediate in density between purified Atlantic Ocean water and water condensed from the atmosphere. Within the experimental error the entire difference in density between fresh and salt water appears to be due to differences in the oxygen isotopic ratios. The bearing of these results on theories explaining the relatively large concentration of O¹⁸ in the atmosphere is discussed.

IN applying¹ the isotopic exchange theory of Urey and Greiff² to the interpretation of the relatively large concentration of O¹⁸ in the atmosphere, the author estimated that of the difference in density between purified salt water and fresh water amounting to 1.9 p.p.m. ap-

proximately 1.6 p.p.m. was due to a difference in the isotopic ratio of oxygen. Greene and Voskuyl³ state, "yet it is improbable that more than 1 p.p.m. . . . is due to the oxygen isotopes." There is also the possibility that fresh water might have the same isotopic composition as atmospheric water vapor. In order to answer these questions

¹ M. Dole, *J. Chem. Phys.* **4**, 268 (1936).

² H. C. Urey and L. J. Greiff, *J. Am. Chem. Soc.* **57**, 321 (1935).

³ C. H. Greene and R. J. Voskuyl, *J. Am. Chem. Soc.* **58**, 693 (1936).