

The Raman Spectra of Water, Aqueous Solutions and Ice

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The Raman Spectra of Water, Aqueous Solutions and Ice

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(Received November 9, 1936)

The Raman spectra of water at different temperatures, of aqueous solutions and of ice have been discussed in detail. Several low frequency shifts such as $\Delta\tilde{\nu}$ 150, 445 and the shift at 2170 are easily discernible if ultraviolet excitation is used. The first two of these vary markedly in intensity with temperature changes and are affected by some solutes. All three are present in ice at slightly displaced frequencies. At least some of these frequencies may be ascribed to the intermolecular influences. Whatever may be the mechanism of polymerization or association these results indicate that effectively such a state exists and is a function of environmental conditions.

INTRODUCTION

THE most consistently divergent results in any Raman spectra studies have been those obtained from the investigation of water. This is primarily attributable to the unique broadness of the bands observed. Theoretically water vapor has three fundamental frequencies, namely, $\Delta\tilde{\nu}$ 1595 (δ_r) for the transverse oscillation or the bending motion of the hydrogen atoms, $\Delta\tilde{\nu}$ 3600 (ν_r) for their symmetrical oscillation in a linear direction along the line of the valence bonds and $\Delta\tilde{\nu}$ 3757 (ν_s) for the asymmetrical oscillation of the atoms in the molecules. Part of the difficulty has been that not all of these are active either in infrared absorption spectra or in Raman spectra. Furthermore, from the latter point of view there appear possibly three bands in the $\Delta\tilde{\nu}$ 3400–3600 region for the liquid. This is not observable in the infrared absorption as the dipole moment change is small. On the other hand, $\Delta\tilde{\nu}$ 3756 is not observed at this frequency in the Raman spectra for either the liquid or vapor but appears as $\Delta\tilde{\nu}$ 3630 in the liquid and 3654 in the vapor. The conclusion possibly has been reached that the multiplicity of bands observed in liquid water owe their origin to the existence of several molecular species, the interaction giving rise to a perturbation of the normal frequency shifts. Whether or not they are physically distinct species or are the result of hindered rotation or translation is still unsettled. The effect, however, in either case is that the interaction between adjacent water molecules is far from negligible and there is a pronounced effect upon the Raman spectra obtainable. This is supported in no small degree by the existence

of other Raman shifts in the frequency range between $\Delta\tilde{\nu}$ 60 and 1600 which cannot be accounted for by the vibrations of a classical oscillator of the type XY_2 .

HIGH FREQUENCY SHIFTS FOR THE WATER BANDS

The results obtained up to 1934 have been summarized in detail by the writer.¹ The earlier work, principally by I. R. Rao, indicated three Raman frequencies in the region of $\Delta\tilde{\nu}$ 3220, 3420 and 3630 corresponding to the symmetrical vibrations of the hydrogen atoms. The exact maxima estimated by visual inspection by different observers varied over a range of 50 or more wave numbers. The advent of more accurate determinations through microphotometric means has materially reduced the discrepancies.

Unfortunately from the point of view of simplicity of interpretation neither the intensity nor the maxima of the bands $\Delta\tilde{\nu}$ 3220–3630 remain constant. They are influenced both by dissolved electrolytes and temperature. Rao,² Meyer³ and Ganesan and Venkateswaran⁴ early observed that an increase in temperature caused a diminution in the intensity of $\Delta\tilde{\nu}$ 3220 frequency and an increase for $\Delta\tilde{\nu}$ 3630. The opposite effect has been observed in going from water to ice. The effect of solutes is generally somewhat similar to that of a temperature increase.^{5–7} The evidence for the

¹ Hibben, *Chem. Rev.* **13**, 345 (1933).

² Rao, *Indian J. Phys.* **3**, 123 (1928).

³ Meyer, *Physik. Zeits.* **31**, 510 (1930).

⁴ Ganesan and Venkateswaran, *Indian J. Phys.* **4**, 195 (1930).

⁵ Hibben, *Proc. Nat. Acad. Sci.* **18**, 532 (1932).

⁶ Brunetti and Ollano, *Atti accad. Lincei* **12**, 522 (1930).

⁷ Ollano, *Zeits. f. Physik* **77**, 818 (1932).

existence of a band at $\Delta\bar{\nu}$ 3630 is dependent mainly upon a very small break in the curves concomitant with a marked shift in the position of the central band. It is difficult, therefore, to decide whether this is indicative of a change in the position of the maxima of the band or an augmentation in the intensity of the highest frequency. Early observers and more recently Magat⁸ failed to observe any band at $\Delta\bar{\nu}$ 3630. On the other hand, Carelli and Cennamo⁹ consider the principal water band made up of three components $\Delta\bar{\nu}$ 3110, 3400 and 3590. The extensive work of I. R. and C. S. Rao¹⁰⁻¹³ also indicates three bands.

LOW FREQUENCY SHIFTS FOR THE WATER BANDS

Segrè,¹⁴ Bolla,¹⁵ Magat^{16a, b} have indicated frequencies less than $\Delta\bar{\nu}$ 1600. These are $\Delta\bar{\nu}$ 60, 140-172, 510-780. From the published microphotometric curves the frequencies of $\Delta\bar{\nu}$ 60 and 780 are very doubtful, as will be seen later. Nevertheless it is of considerable importance to confirm the existence of these and other frequencies mentioned and this has been one of the purposes of this investigation. There is no doubt that low frequency oscillations do exist at $\Delta\bar{\nu}$ 150

and 445.* This is likewise true of $\Delta\bar{\nu}$ 2170, the last frequency having been noted before only by Bolla.¹⁷ Owing to their extreme weakness none of the frequencies below $\Delta\bar{\nu}$ 3220 was observed with accuracy until the advent of ultraviolet excitation, although it was postulated⁶ that a frequency at $\Delta\bar{\nu}$ 1600 should exist, and indeed it was early observed by Kimura and Uchida¹⁸ and by da Silveira.¹⁹ The $\Delta\bar{\nu}$ 500-700 band is claimed by Magat²⁰ to show an anomalous disappearance at 37°C. This is disputed by Bolla.²¹

Other shifts supposedly observed, namely, $\Delta\bar{\nu}$ 3990,¹⁷ 984,²² 2355,⁴ 4023 and 5100⁸ and a group observed by Hulubei²³ extending from $\Delta\bar{\nu}$ 6747 to 10944 have been postulated but are doubtful.

At least one low frequency shift occurs in liquid D₂O, namely, $\Delta\bar{\nu}$ 178 in water.²⁴⁻²⁶ This is not appreciably displaced from its position. On the contrary the high frequencies in the $\Delta\bar{\nu}$ 3400-3600 group are shifted very much lower in D₂O. Depolarization measurements on water and deuterium oxide by Ananthakrishnan²⁴ indicate

* The determination of the absolute maximum of a band located on the downward slope of a larger band is subject to considerable error. The maxima as given here differ slightly from those estimated by others. This is without great significance.

¹⁷ Bolla, *Nuovo cimento* **10**, 101 (1933).

¹⁸ Kimura and Uchida, *Japan J. Phys.* **5**, 97 (1928).

¹⁹ da Silveira, *Comptes rendus* **195**, 652 (1932).

²⁰ Magat, *J. de phys. et rad.* **6**, 179 (1935).

²¹ Bolla, *Nuovo cimento* **12**, 243 (1935).

²² Johnston and Walker, *Phys. Rev.* **39**, 535 (1932).

²³ Hulubei, *Comptes rendus* **194**, 1474 (1932).

²⁴ Ananthakrishnan, *Proc. Indian Acad. Sci.* **3A**, 201 (1936).

²⁵ Ananthakrishnan, *Proc. Indian Acad. Sci.* **2A**, 201 (1935).

²⁶ Magat, *Comptes rendus* **201**, 667 (1935).

TABLE I. Raman spectra of water, ice, solutions and hydrates.

| WATER | | | | ICE | NaOH 1 molal | NaOH 1.4 molal | Ba(OH) ₂ 0.175 molal | LiCl 7.1 molal | KBr 2.8 molal | MgCl ₂ 1.7 molal | MgCl ₂ · 6H ₂ O | CdSO ₄ · 8/3H ₂ O† | | | | | |
|-------------------|----------|-------------------|----------|-------------------|-----------------|-------------------|------------------------------------|-------------------|------------------|--------------------------------|------------------------------------------|---------------------------------------------|----------|------|------|------|-----|
| 28° | 88° | | | | | | | | | | | | | | | | |
| $\Delta\bar{\nu}$ | <i>i</i> | $\Delta\bar{\nu}$ | <i>i</i> | $\Delta\bar{\nu}$ | <i>i</i> | $\Delta\bar{\nu}$ | <i>i</i> | $\Delta\bar{\nu}$ | <i>i</i> | $\Delta\bar{\nu}$ | <i>i</i> | $\Delta\bar{\nu}$ | <i>i</i> | | | | |
| 144 | (1) | 149 | (00) | 205 | (4) | 145 | (00) | 160 | (0) | 150 | (2) | 128 | (2) | | | | |
| 440 | (4) | 450 | (2) | 601 | (3) | 450 | (1) | 450 | (0) | 450 | (2) | 465 | (4) | 474 | (4) | | |
| 1627 | (3) | 1629 | (3) | — | | 1629 | (2) | 1629 | (0) | 1629 | (2) | 1630 | (5) | 1625 | (4) | | |
| 2170 | (2) | 2118 | (3) | | | 2140 | (1) | 2140 | (0) | 2135 | (1) | — | 2157 | (3) | 2165 | (3) | |
| | | | | 2225 | (2) | | | | | | | | | | | | |
| | | | | 3136 | (10) | | | | | | | | | | | | |
| 3219 | (8) | 3222 | (5) | 3330 | (8) | 3220 | (7) | 3216 | (5) | 3215 | (9) | 3236 | (5) | 3206 | (7) | 3202 | (7) |
| 3445 | (10) | 3460 | (10) | | | 3450 | (10) | 3460 | (10) | 3450 | (10) | 3471 | (10) | 3450 | (10) | 3372 | (8) |
| | | | | | | | | | | | | | | | | 3346 | (5) |
| | | | | | | | | | | | | | | | | 3424 | (8) |
| | | | | | | | | | | | | | | | | 3514 | (8) |

† The shifts for cadmium sulfate proper are not included in this table. There is no evidence for any un-ionized magnesium chloride.

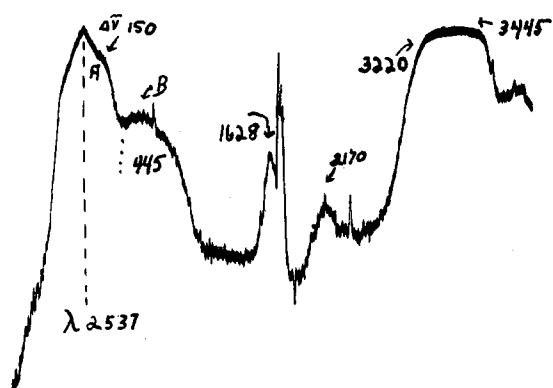


FIG. 1(a) The principal Raman bands for water excited by the 2537A mercury line, namely, $\Delta\bar{\nu}$ 150, 445, 1628, 2170, 3220, 3445, which are, from left to right, indicated by arrows.

Fig. 1 (a) shows four different water bands in addition to the $\Delta\bar{\nu}$ 3220–3630 shifts. These are: $\Delta\bar{\nu}$ 150, 445, 1628, 2170. That $\Delta\bar{\nu}$ 150 is genuine is indicated in 1 (b) which shows an expanded tracing of this portion of the band. Fig. 2 shows the effect of temperature on the lower frequency bands. Fig. 3 shows the remarkable effect of adding small quantities of alkali. Fig. 4 indicates the effect in 2.8 molal solution of KBr, 1.7 molal MgCl_2 , and 7.1 molal LiCl, respectively, and Fig. 5 shows the water bands in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ crystals whose shifts are, respectively, $\Delta\bar{\nu}$ 3387 and 3507, 3348 and 3426. In the last illustration are shown the results of experiments with ice, including the shifts at $\Delta\bar{\nu}$ 205, 601 and 2225 (Fig. 6).

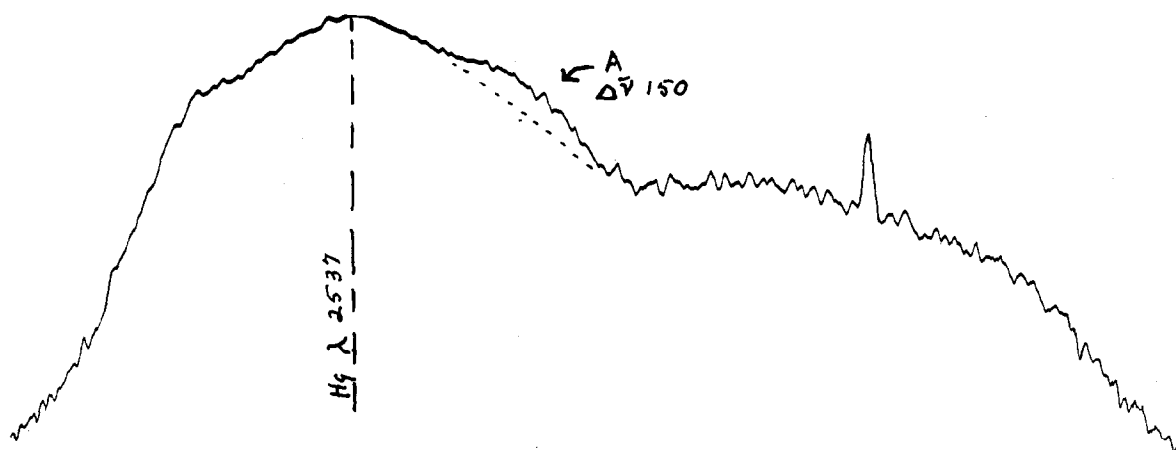


FIG. 1(b). Enlarged microphotometer tracing of that portion of the curve indicated by band A in (a).

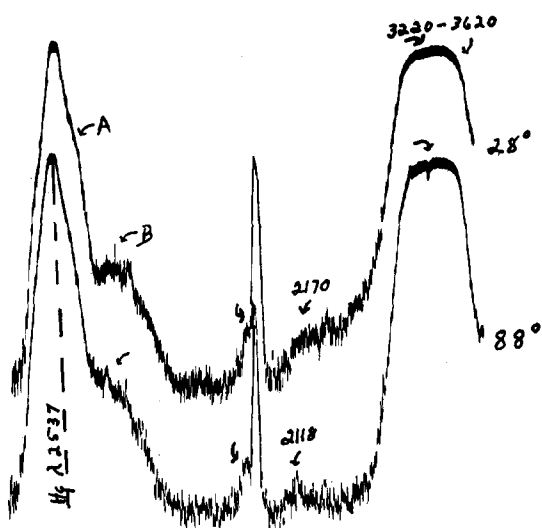


FIG. 2. The decrease in intensity of the water bands $\Delta\bar{\nu}$ 150 and 445 as a function of increased temperature is indicated.

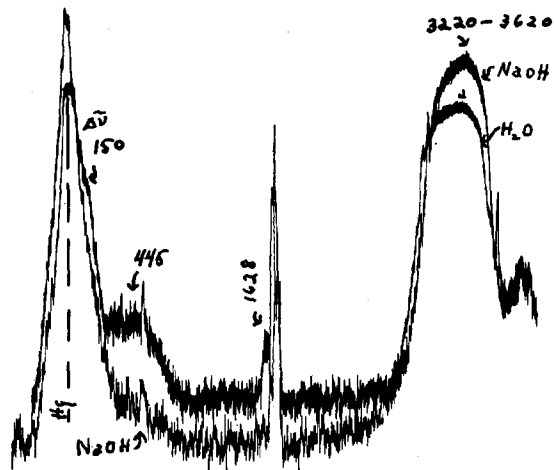


FIG. 3. A comparison between the Raman spectrum of pure water and a 5 percent solution of NaOH.

an increase in the value of ρ with an increase in the frequencies of the Raman shifts in this region. Consequently $\Delta\bar{\nu}$ 3630 should correspond to the ν_e —the asymmetrical type of vibration. The $\Delta\bar{\nu}$ 178 (150) also has a maximum depolarization.

STRUCTURE OF WATER

The modification of the Raman frequencies with varying temperatures and solutes has been the subject of investigation by I. R. Rao,¹⁰ C. S. Rao,¹² Segrè,¹⁴ Hatley and Callihan,²⁷ Specchia²⁸

²⁷ Hatley and Callihan, *Phys. Rev.* **138**, 909 (1931).

²⁸ Specchia, *Nuovo cimento* **7**, 388 (1930).

and others. In general the observations have been confined to the $\Delta\bar{\nu}$ 3200–3600 band. The explanation of the modifications in this band is largely based on a change of the number of water polymers, i.e., such as H_2O , $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$, the normal unpolymerized water giving rise to the high frequency shift $\Delta\bar{\nu}$ 3630 (cf. $\Delta\bar{\nu}$ 3654 for water vapor). Bernal and Fowler²⁹ have proposed a quasicrystalline arrangement for water having respectively a tridymite, quartz and close-packed ideal structure as a function of increasing temperatures. The difference between these con-

²⁹ Bernal and Fowler, *J. Chem. Phys.* **1**, 515 (1933).

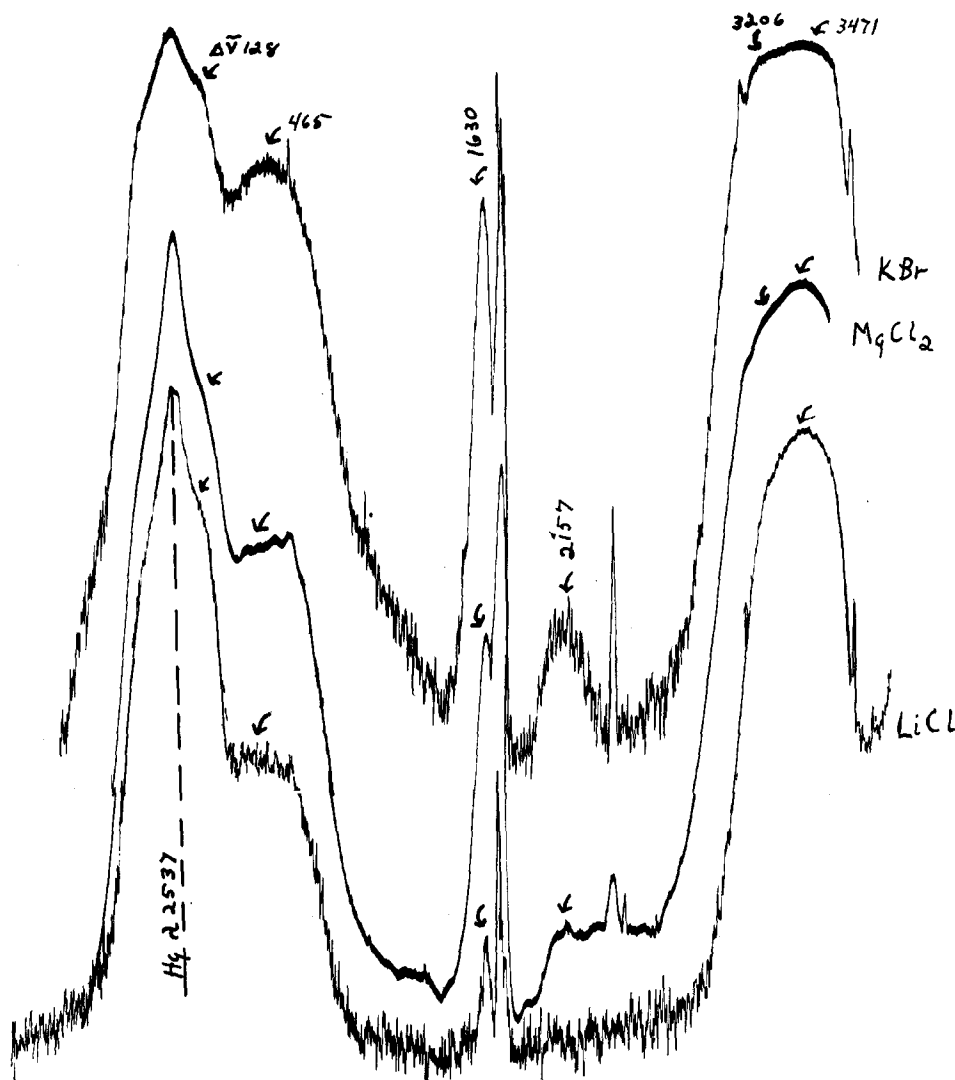


FIG. 4. A comparison between solutions of 2.8 molal KBr, 1.7 molal MgCl_2 , and 7.1 molal LiCl . There is no marked difference between these curves and that for pure water taken under the same conditions.

cepts is more illusory than real. The essential fact is that in either case there will be a profound influence on the Raman spectra as the changes in the constitution of the water take place.

EXPERIMENTAL RESULTS

The object of the experimental work to be described was first, to clarify some of the discrepancies in the reported Raman frequencies and, second, to investigate the "association" of water with particular emphasis on those lines which should be most sensitive to intermolecular perturbation—the low frequency shifts. The studies have been carried out on water at different temperatures, on crystal hydrates, solutions and ice.

It should be pointed out that the experimental procedure employed is of paramount importance. Microphotometric curves alone are without great significance. In these experiments it has been attempted to reproduce the conditions of illumination so that the same number of quanta strike the same number of water molecules under comparable conditions. On each plate developed a

reference standard of the water spectrum was also made. The maximum and minimum excursions of the galvanometer while tracing the plates were adjusted so as to give the same displacement. Without such precautions it is easily possible to confuse the experimental results and subsequent interpretations.

For those substances, such as acetic acid, and solutions of lithium chloride, which showed some absorption in the ultraviolet, it is necessary to take this absorption into account. These results are *not* indicative of small changes in scatterings. It is only when the modifications have reached a degree considerably beyond the experimental error that they have been held to be significant.

The results are indicated graphically in the accompanying figures, and tabularly in Table I.

DISCUSSION

It is to be noted that the shifts at $\Delta\bar{\nu}$ 150 and 445 in water decrease in intensity with an increased temperature and $\text{O} \leftrightarrow \text{H}$ shifts are at least two in number, $\Delta\bar{\nu}$ 3220 and 3445. The maximum of the last band shifts to a higher frequency with an increase in temperature and the intensity of the $\Delta\bar{\nu}$ 3220 simultaneously diminishes. It is not possible from these or other curves obtained in the course of this investigation to say with certainty that $\Delta\bar{\nu}$ 3630 is present.

The addition of any NaOH and $\text{Ba}(\text{OH})_2$ markedly diminishes the intensity of the low frequency shifts whose very existence can be solely attributed to intermolecular interaction.

Apparently, therefore, the function of the hydroxyl ion is to decrease polymerization rather than to increase hydration. The low frequency bands are nearly completely eliminated with a 1.4 molal solution of sodium hydroxide and are markedly diminished with a 1.0 molal solution. A 0.175 molal solution of barium hydroxide also diminishes the intensity of these bands, but in a lesser degree. It is evident that one hydroxyl ion is capable of depolarizing a large number of water molecules. This seems to be at variance with the hypothesis of Bernal and Fowler,²⁹ who indicate that an OH ion should give greater coherence to the water structure.

The effect of salts containing both large and small anions and cations on the water is not marked. The frequency shifts $\Delta\bar{\nu}$ 150 and 445

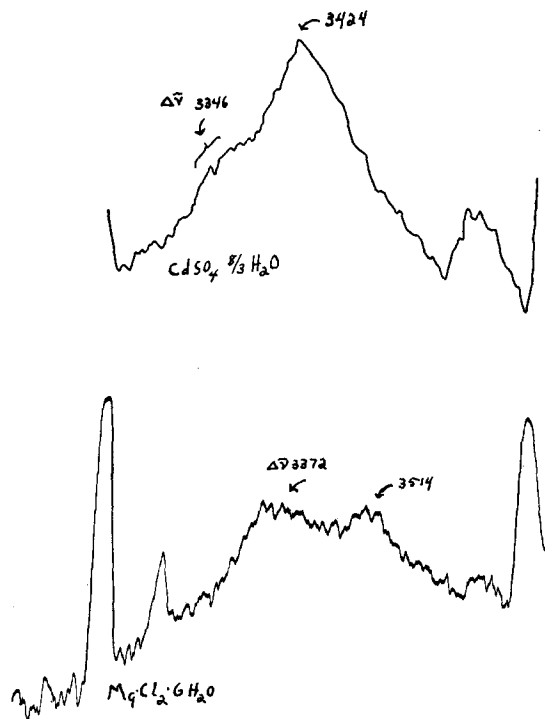


FIG. 5. Water of crystallization in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$ yields two lines each corresponding to the $\text{O} \leftrightarrow \text{H}$ oscillation, but differing markedly both in the magnitude of the displacement and the relative intensities.

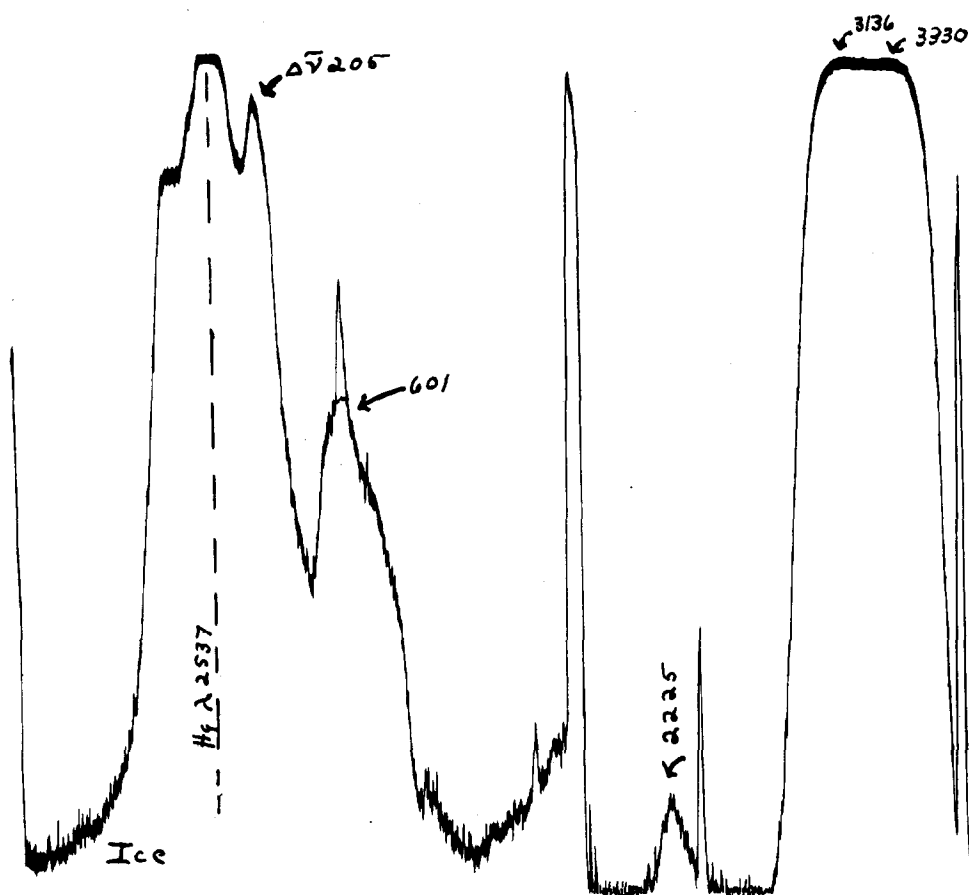


FIG. 6. The Raman spectrum of ice showing the enhancement in intensity of some of the shifts as a result of intermolecular interaction.

persist in solutions of magnesium chloride, lithium chloride and potassium bromide. The accuracy of intercomparing these curves is not sufficiently great to warrant a definite statement of the relative effects of these compounds. As compared with the alkali hydroxides, however, the difference is very marked.

Any expected effect as to the lowering of the structural temperature of the solution by ions of small radii, as postulated by Bernal and Fowler, is not realized. The persistence of the frequencies whose origin is attributed to intermolecular effects in these solutions does not point to any pronounced dissociation of the structural complex with large ions or any pronounced increase in regularity of arrangement with small ions.

The band occurring at $\Delta\bar{\nu}$ 2118 may be a result of the combination between $\Delta\bar{\nu}$ 445 and the fundamental at $\Delta\bar{\nu}$ 1629. It is also interesting to note that this frequency is nearly equal to the

difference between the fundamental at $\Delta\bar{\nu}$ 3756 active in the infrared and inactive in Raman spectra and a combination of two $\Delta\bar{\nu}$ 1650 frequencies ($\nu_o - 2\delta_\pi$).

Further evidence for the assignment of the low frequency vibrations (hindered translation and rotation) to intermolecular complexes is obtained from the spectrum of ice which is known to be polymerized. In addition to the frequencies noted by others there appear $\Delta\bar{\nu}$ 205, 601, 2225. The first two of these are obviously slightly shifted frequencies occurring in water and appear with great strength, the first frequency showing an anti-Stokes line.

The spectra obtained from water of hydration do not have maxima identical with those of liquid water and the maxima alter from crystal to crystal. For the hexahydrate of magnesium chloride there appear two maxima, $\Delta\bar{\nu}$ 3372 and 3514 of nearly equal intensity. For cadmium sulfate

8/3 hydrate the maxima are, respectively, $\Delta\bar{\nu}$ 3346 and 3424 with a great disparity in intensities of the two shifts. The influence of the configuration of the crystals is evidently reflected in a change in force constant between the hydrogen and oxygen atoms.

The accuracy of determining the maxima of the extremely broad O \leftrightarrow H oscillations does not permit too much weight to be placed on reasonable variations in the magnitude of these shifts. This may be said also of the lowest frequencies. In the case of ice, however, there is a genuine displacement of the maxima, and the change in the magnitude of $\Delta\bar{\nu}$ 2170 between hot and cold water is likewise real.

SUMMARY

The Raman shifts obtained from water, ice and some solutions have been investigated particularly from the point of view of the low frequency oscillations. These could not be present

in the spectrum of a simple unhindered triatomic molecule and their existence is explicable only as a result of intermolecular interaction regardless of the precise mechanism of such interaction. The greatly enhanced intensities of these lines in ice as compared with water furnish reasonably conclusive evidence that the assignment of these frequencies to intermolecular coupling is proper. Moreover their alteration in intensity in the liquid phase with temperature variations is consistent with the concept of structural changes in the liquid as a function of temperature. In solution, however, the results are not in entire agreement with the lowering of the structural temperature of the solutions by ions of small radii or with an equivalent elevation in temperature by ions of large radii. New frequencies are reported for ice and the existence of a shift at $\Delta\bar{\nu}$ 2170 for water has been found to be genuine. Other low frequencies noted by a few observers have been confirmed.

Infrared Absorption Spectra of Four Grignard Solutions*

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Southwestern College, Winfield, Kansas

(Received May 18, 1936)

Absorption spectra are reported for twelve liquids: four typical Grignard solutions, and eight related substances, for the range 1.0 to 13 μ . Absorption frequencies at 784, 910, 4250 and possibly 1950 cm^{-1} appear to be associated with compounds which contain magnesium. Possible origins of these frequencies are discussed.

INTRODUCTION

THE infrared absorption spectra of twelve compounds, including four typical Grignard solutions, are reported in this paper, for the range from 1 μ to 13 μ . The primary purpose of the work was to determine the wave-lengths at which selective absorption occurs, in several Grignard compounds. This work is part of a broad study of a number of the physical properties of such compounds, which has been carried on under the leadership of Professor R. T. Dufford; it is

hoped that eventually it may prove to be possible to correlate these properties with the very interesting photovoltaic effects which have been shown¹ to exist in solutions of Grignard compounds.

Grignard compounds are prepared in anhydrous ethyl ether solution, by the action of magnesium metal on various organic halides.

TABLE I.

| Region | Wave-lengths | Cell Thickness | Slit Width |
|--------|----------------|----------------|------------|
| 1. | 1.0- 1.9 μ | 1.00 cm | 0.025 cm |
| 2. | 1.9- 4.5 μ | 0.032 cm | 0.030 cm |
| 3. | 4.5- 9.0 μ | 0.026 cm | 0.035 cm |
| 4. | 9.0-13.0 μ | 0.016 cm | 0.065 cm |

* Abstracted from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Missouri.