

RAMAN SPECTRA IN INORGANIC CHEMISTRY

JAMES H. HIBBEN

*Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D. C.*

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I. INTRODUCTION

There are few physical discoveries which have resulted in a greater stimulation to investigations in a particular field than the discovery of the Raman effect by Sir C. V. Raman in 1928. Since that time there have appeared more than a thousand publications, each of which has usually discussed the Raman effect in connection with different compounds. In reviewing the subject briefly it is necessary, therefore, to set some arbitrary limitations to the material to be covered. Except in specific cases, discussions in this review will be limited to the more or less characteristic developments since 1930, it being assumed that the references and data given in Kohlrausch's "Der Smekal-Raman Effekt" (3) and the summaries by Ganesan (2) and Bhagavan-tam (1) will cover the material prior to that time, while the bibliography by Sirkar (6) will be supplementary.

Other arbitrary distinctions may be made, namely, theoretical aspects of the Raman effect, physical aspects, and empirical investigations. The first of these is considered to deal with the more strictly spectroscopic applications of the Raman effect, that is, the information which may be gained in regard to the various energy levels of a molecule.

So far as these applications are concerned, they are naturally intimately connected with band spectroscopy, which has been discussed in detail by Mulliken (4, 5) and by Villars (7) in This Journal. Raman spectra, however, are concerned with a more limited field, dealing mainly only with the vibrational and rotational transitions of a given system and rarely, if ever, with elec-

tronic transitions. The selection rules governing these transitions, however, are not identical with those governing infra-red absorption, which is likewise chiefly concerned with vibrational and rotational transitions, so that corollary information of value is obtainable from the Raman effect. Furthermore, because of their comparative simplicity and the relative strength of fundamental vibrations as compared to harmonics, Raman spectra are interpreted much more easily than infra-red or visible band spectra.

In the physical applications there might be classed the information that Raman spectra give as to spacial distributions of atoms and molecules, specific heats, electric moments, Boltzman distributions, and other more strictly physical properties.

Empirical investigations may be classified in two parts—organic and inorganic chemistry—with, however, the usual overlapping between these two subdivisions. For the purpose of this review the inorganic subject matter will be dealt with first and the organic reserved for later publication. The same principles apply to both fields of investigation, in particular the extrapolation of logical conclusions from one field to the other. Nevertheless, there is sufficient demarcation between these two general subdivisions of chemistry to warrant their separate treatment, both from the point of view of the material to be covered and because of a somewhat different emphasis in the two lines of investigation.

Empirical observations deal with the observed values of Raman lines (often referred to as modified lines, Raman shifts, frequency displacements, and Raman rays). These have yielded many interesting and fruitful results pertaining to the constitution of organic compounds and inorganic compounds in solutions, vapors, solids, and liquids, and have a much wider application than is obtainable from strictly theoretical considerations. From the latter point of view, alone, Raman spectra suffer equally with band spectra, quantum mechanics, and, to a certain extent, infra-red absorption spectra, the limitations imposed by being practically applicable only to relatively simple molecules according to chemical concepts.

While susceptible to modification on the basis of accumulation of new data, these empirical observations, however, are now based on a sufficiently large number of statistical observations to contain more than an element of truth and to carry the same weight as any experimentally determined fact. Their interpretation is, however, a matter of opinion and can be viewed as correct only in the degree of reasonableness by which it explains known facts. This type of observation has, in the main, been extremely consistent with known chemical and physical behavior. There are, however, many interesting cases where the Raman results have been either divergent or applicable where no other method will yield results.

This procedure is particularly advantageous in the case of solutions, about whose complexity little is known, in the study of polymers and of amorphous solids, and in the chemical constitution of organic and inorganic compounds whose structure is open to question. It is for this reason that the discussion of empirical observations will be given the greatest weight in this summary.

DEFINITION OF TERMS

The most commonly used method of expressing Raman shifts is in terms of wave numbers or the number of vibrations per centimeter. Since the Raman lines are generally regarded as frequency differences, it is more or less customary to employ $\Delta\bar{\nu}$ to express this. The actual frequency (vibrations per second) of any Raman line is given by the expression $\nu\lambda = 3 \times 10^{18}$, where the digits represent the velocity of light in Ångström units (Å. or A. U.), and λ is the wave length, also expressed in Ångström units. In wave numbers per centimeter (number of waves per centimeter) this becomes

$$\bar{\nu} = \frac{10^8}{\lambda_{(\text{A.U.})}}$$

where $\bar{\nu} = \nu/c$. The term c is the velocity of light in centimeters per second (3×10^{10}). $\Delta\bar{\nu}$ is obtained from the following:

$$\bar{\nu}_1 - \bar{\nu}_2 = \pm \Delta\bar{\nu}$$

where $\bar{\nu}_1$ are the wave numbers per centimeter of the exciting radiation and $\bar{\nu}_2$ the wave numbers per centimeter of the Raman radiation.

In the case of frequencies as calculated from *mechanical* models, expressed in terms of wave numbers per centimeter, these are sometimes given as $\bar{\nu}$, since this term in these models represents an actual frequency and not a frequency difference. The numerical value of $\bar{\nu}$ thus calculated is theoretically equivalent to $\Delta\bar{\nu}$ obtained from spectroscopic data. However, for the sake of convenience in deriving the frequency terms arising from different molecular configurations, the letter n will frequently be used in place of $\bar{\nu}$. (See equation 4, for example.) It is related to $\bar{\nu}$ by the following equation:

$$n^2 = 5.87 \times 10^{-2} \cdot \bar{\nu}^2$$

Experimentally observed Raman shifts will be given in wave numbers per centimeter, as for example, $\Delta\bar{\nu} = 296 \text{ cm.}^{-1}$, or, more simply, $\Delta\bar{\nu} 296$. In particular instances it may also be of advantage to express the Raman shifts in terms of the corresponding wave length in the infra-red. This is related to $\Delta\bar{\nu}$ (in cm.^{-1}) by the following expression:

$$\Delta\bar{\nu} = \frac{10^4}{\lambda_\mu}$$

where lambda (λ) is expressed in μ or 10^{-4} cm.

The exciting radiation giving rise to the Raman lines will be expressed in round numbers in terms of Ångström units. It is usually impossible to say whether any of the recorded values of Raman shifts are corrected to vacuum or not.

Other terms employed are $\bar{\mu}$, representing the reduced mass, that is

$$1/\bar{\mu} = 1/m_1 + 1/m_2$$

where m_1 and m_2 , etc., are the atomic weights of the vibrating masses in a mechanical system. This may also be written

$$\frac{1}{\bar{\mu}} = \frac{1}{M} + \frac{1}{m}$$

where M and m have the same significance as m_1 and m_2 . Further, for the sake of convenience the relation $(M + 2m)/m$ may be abbreviated as p .

F is the elastic restoring force or the force per unit displacement expressed in dynes per centimeter.

d is the deformation force constant in dynes per centimeter.

h is Planck's constant, 6.54×10^{-27} erg seconds.

N is Avogadro's number, 6.06×10^{23} .

ρ is the degree of depolarization.

k is the Boltzmann constant, 1.37×10^{-16} erg per degree.

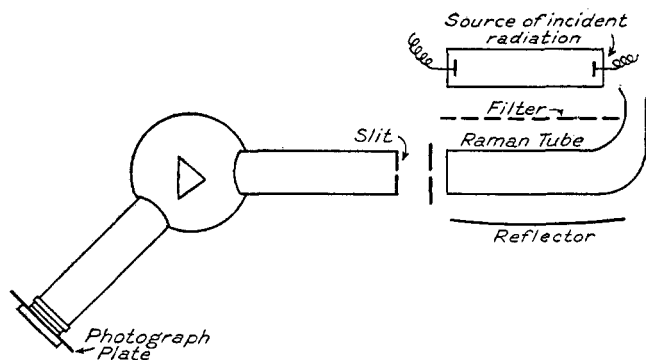


FIG. 1. SCHEMATIC DIAGRAM OF RAMAN APPARATUS
Showing spectrograph, Raman cell, exciting source, reflectors, and filters

II. THEORY

A. THE ORIGIN AND MAGNITUDE OF RAMAN FREQUENCY SHIFTS

The first approach to this subject is to discuss the method employed to produce the Raman effect. Essentially the method is to irradiate the substance to be examined with radiation as nearly monochromatic as possible. The material traversed by the light beam becomes a seat of emission, particularly observable in a direction normal to the incident beam. This light emerges at right angles to the incident radiation, enters the slit in the spectrograph, and is registered on a photographic plate. This arrangement is depicted schematically in figure 1. This emergent or "scattered" light may owe its origin to several causes, namely,

“Rayleigh” scattering from particles of colloidal size and molecules themselves, if the material is homogeneous, direct reflection if it is inhomogeneous, fluorescent emission if fluorescence is possible, and true Raman scattering. Frequently all of these factors are simultaneously operative.

The principal emissions are due to Rayleigh scattering and reflection. These result, however, in no alteration of the incident spectrum, and the lines thus recorded are merely those belonging to the incident radiation. Fluorescence and Raman spectra are secondary effects and result in the emission of light different from that to which they owe their origin, a phenomenon which has long been known in the domain of x-rays (Compton effect).

In the optical phenomenon known as the Raman effect, the quantum of light colliding with the molecule of the irradiated material is debased, that is, it loses some of its energy to the molecule in the same fashion as any inelastic collision involving a quantum process.

This energy is absorbed as increased vibrational and rotational energy, and the resultant light scattered or emitted is *usually* of greater wave length than the impinging light by a definite amount, according to the quantum process involved. However, if the molecule is in a higher energy state than its normal state, the emitted light *may* have greater frequency or shorter wave length than that of the exciting source, resulting in what are sometimes called “anti-Stokes” lines. In either case the lines which thus appear are not present in the original radiation and are a function of the molecular constitution of the irradiated substance.

This conception of an interaction of a light quantum and a molecule to produce modified radiation is not new. It was postulated by Smekal (67) and is embraced by the Kramers-Heisenberg dispersion theory (35). Experimentally, however, such observations were first made by Raman (55), and treated shortly thereafter by Cabannes (19), Landsberg and Mandelstam (37, 38), and Rocard (59). The next consideration is the relation between absorption and emission in these processes.

Infra-red absorption and the Raman effect

The above conception of photon collision may be arithmetically represented as follows:

If E_l and E_k represent two energy levels of a molecule, the frequency $\nu_{l,k}$ given by the quantity $(E_l - E_k)/h$ may manifest itself in a scattered spectrum giving rise to various Raman lines represented by $\nu_0 \pm \nu_{l,k}$, where ν_0 is the frequency of the incident quantum of radiation.

Actually, however, there are certain limiting conditions: Raman lines do not always correspond to infra-red absorption bands, as this would indicate. It has been pointed out by Langer (40, 41) and by Dieke (27) that it is necessary to start with molecules not in a single "eigen" state but with the system capable of being excited in two of its characteristic states represented by l and k , and that transitions should be possible for the molecules from either of these states to a third energy level represented by n . It is immaterial whether the transitions from l to k are forbidden or not. If the transition $\nu_{l,k}$ is forbidden, there would be no absorption corresponding to this frequency, whereas if a third discrete level n exists to which transitions from l and k may take place, the same $\nu_{l,k}$ would give rise to a Raman line. On the other hand, if no n (common third level) exists, an absorption line would be present corresponding to $\nu_{l,k}$, but not a Raman line. This may be also expressed as

$$A_{kn}A_{kl} \left[\frac{1}{\nu_{kn} \pm \nu_0} + \frac{1}{\nu_{ln} \pm \nu_0} \right] (\nu_{kl} \pm \nu_0)^2 \quad (1)$$

where A_{kn} is a matrix element for $\int r \psi_k \psi_n dx$, which describes the intensity of the transition between the states k and n giving out radiation

$$\nu_{kn} = \nu_k - \nu_n = \frac{E_k - E_n}{h} \quad (2)$$

The modified frequencies $\nu_{kl} \pm \nu_0$ differ from the incident frequency ν_0 not by an absolute amount but by differences between these; that is, only when two allowable transitions A_{kn} and A_{ln} (different from zero) have a common level n is there any intensity in the scattered frequency.

The Raman shifts as compared with the infra-red absorption in carbon tetrachloride are indicated in figure 2, where the vertical dotted lines represent the Raman transitions and the vertical solid lines the infra-red absorption. This is somewhat idealized. It may be pointed out that while a non-concordance of a few wave numbers between infra-red absorption and Raman spectrum lines may have vital significance to a physicist, a small difference is of

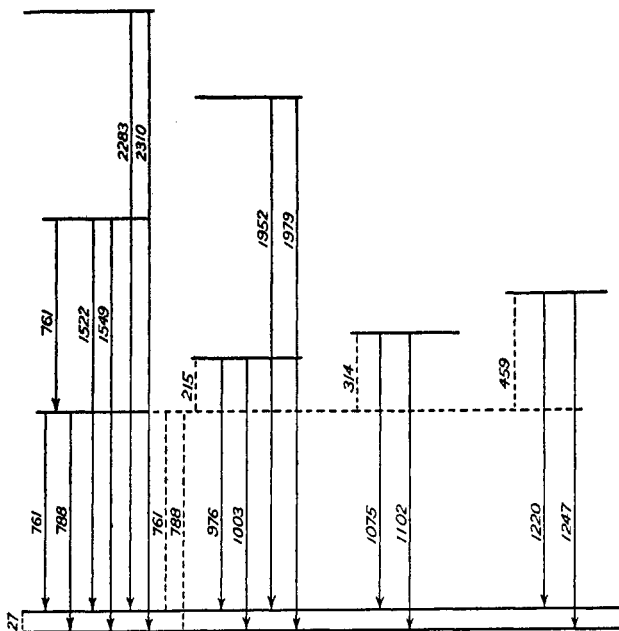


FIG. 2. TRANSITIONS GIVING RISE TO RAMAN LINES AND INFRA-RED ABSORPTION

The vertical dotted lines represent the possible Raman lines. The corresponding $\Delta\nu$ are indicated numerically (after Langer).

little moment to the chemist from the point of view of identification of a given transition for analytical purposes.

In the case of simple molecules it is possible to state *a priori* which frequencies would appear as Raman lines and which as absorption lines, and which others may appear as both, as has been demonstrated by Rasetti (58). The intensity of the Raman emission is dependent in part on the symmetry character of the

initial and final states and on the classical electric moment. Symmetrical oscillations cannot affect the electric moment and the frequency is therefore termed "*inactive*," and cannot appear, except in combination, associated with an unsymmetrical vibration or "*active*" frequency. (These are also termed optically active and inactive.) Since the Raman lines depend for their intensity on the electric moments of interaction with intermediate states, the inactive frequencies are especially favored. Van Vleck (70) considers that the most intense Raman lines are those whose displacements are equal to one of the fundamental frequencies and, second, the Raman lines whose shifts are the harmonics of a fundamental or are combination frequencies. The most intense scattering, however, is the ordinary Rayleigh scattering.

Raman spectra and selection rules

It has already been mentioned that the great majority of molecules are in their normal vibrational states and that transitions, therefore, are mostly characterized by their change from $0 \rightarrow 1$ vibrational quantum numbers. Similarly, Raman spectra may also indicate rotational and rotational-vibrational transitions.

The selection rules in the Raman effect have been determined by Rasetti (58). A discussion of these rules is, in part, a recapitulation of some of the material already mentioned. In order that a shift corresponding to the transition $l \rightarrow k$ may be observed, it is necessary that both states l and k combine at least with a third state n , the Raman spectrum becoming particularly intense when the energy $h\nu_0$ of the impinging quantum is near to $E_n - E_l$. If $E_n - E_l$ equals $h\nu_0$ we have fluorescence instead of the Raman effect.

In the case of a linear molecule in the lowest electronic state and in the J th rotational state ($J = 1, 3, 5, \dots$), it can be said that this state combines only with the $J - 1$ and $J + 1$ rotational states of the upper electronic level. The first of these combines with the J and the $J - 2$ rotational states of the normal electronic level and the second with the J and $J + 2$. So, on the whole,

the possible Raman transitions from the J rotational states to other rotational states are $J \rightarrow J - 2$, $J \rightarrow J$, and $J \rightarrow J + 2$. The second term involves no energy change, that is, gives scattered light of unmodified frequency. The transition involving a degradation of frequency is the $J \rightarrow J + 2$, the remainder giving anti-Stokes lines symmetrical with respect to the exciting lines. Applications of this conclusion will be discussed later in the Raman effect of gases.

Raman effect and molecular configuration

Correlation of the natural frequencies of vibration with molecular structure can be effected by the investigation of the characteristic modes of oscillations of simple polyatomic molecules. This has been done by Dennison (25, 26) for such molecules as carbon dioxide, ammonia, and methane. Bhagavantam (14), from the point of view of Raman spectra, has recalculated the available data for simple molecules of the types X_2 , X_3 , X_4 , AX_2 , AX_3 , and AX_4 , with the assumption that the fields of force are centered around each nucleus, that the displacement of individual particles from their mean position is infinitesimal, that one is concerned only about oscillations around an equilibrium configuration, and that the symmetries of the electron configuration remain essentially undisturbed at the instant of each displacement.

Other calculations have been made by Bates and Andrews (13), Yates (76, 77), Andrews (8, 9, 10, 11), Salant (60, 61), Ellis (29), Kohlrausch (3), Lechner (42), Radakovic (57), and Lespieau, Bourguel, and Wakeman (43).

The theory of force systems of three or more mass particles can be considered only an approximation. Notwithstanding this, however, the application of equations derived from simple systems to more complicated ones has in some cases led to interesting conclusions. That specific quasi-harmonic oscillations exist in complicated molecules has been convincingly demonstrated by dynamic properties of mechanical models (31). Of the several concepts of force systems between mass particles, that of directed bond forces has yielded the most fruitful results. This

was postulated by Andrews (8) on the basis of specific heat values, and it was subsequently pointed out by him (10, 11) that Raman spectra confirmed this hypothesis. This was the first attempt to correlate Raman spectra with molecular vibrations and to indicate that the Raman shifts really gave fundamental natural frequencies.

(a) *Diatomic molecules.* The simplest type of oscillator is one with a single fundamental frequency, such as oxygen, for example ($\Delta\bar{\nu}$ 1555), or chlorine ($\Delta\bar{\nu}$ 556). With molecules of the type of X_2 one can assume a dumb-bell type of molecule, in which the two atoms are held together with a force (F) which may be expressed in dynes per centimeter. If the force is large, the characteristic frequency of vibration will be rapid. If the two atoms are heavy, the characteristic frequency will be slow. From the equation for a simple harmonic oscillator in a mechanical system, one obtains the following relationship:

$$\nu = \frac{1}{2\pi} \cdot \sqrt{F/m} \quad (3)$$

where ν represents the frequency of vibration per second, m the mass of the vibrating components, and F the force exerted between them. In an atomic system, if ν is expressed in wave numbers per centimeter and masses by relative atomic weights, this may be written:

$$\bar{\nu} = \frac{\sqrt{N}}{2\pi c} \sqrt{\frac{F}{\bar{\mu}}} = 4.125 \sqrt{\frac{F}{\bar{\mu}}} \quad \text{or} \quad n = \frac{\bar{\nu}}{4.125} = \sqrt{\frac{F}{\bar{\mu}}} \quad (4)$$

where N is Avogadro's number and c the velocity of light, $\bar{\mu}$ the reduced mass and $n^2 = 5.87 \times 10^{-2} \cdot \bar{\nu}^2$.

To calculate F , this reduces to

$$F = \nu^2 \left(\frac{4\pi^2 c^2}{N} \right) \bar{\mu} \text{ (dynes per centimeter)} = 5.87 \times 10^{-2} \cdot \bar{\nu}^2 \bar{\mu} = n^2 \bar{\nu}^2 \bar{\mu} \quad (5)$$

If F is the restoring force in the system and the greatest amplitude of vibration is \bar{a} , the mean restoring force is $1/2\bar{a}^2 F$, which may be equated to $h\bar{\nu}c$, hence

$$\bar{a} = \sqrt{\frac{hN}{4\pi^2 c}} \cdot \sqrt{\frac{1}{\bar{\mu}\bar{\nu}}}$$

or

$$\bar{a} = 8.2 \times 10^{-8} \sqrt{\frac{1}{\bar{\mu}\bar{\nu}}} \text{ cm.} \quad (6)$$

In the diatomic oscillator, therefore, if one can determine the frequency of oscillation, then the amplitude of vibration and force constant are also calculable. These are only fairly approximate. Nevertheless, from the characteristic frequencies of "inner" vibrations, that is, the oscillations between two given atoms in a molecule (even though that molecule may not be merely a diatomic one), it has been possible to calculate the approximate relative binding force. The amplitude of vibration calculated by this method varies from 0.06 to 0.09 A. U.

(b) *Polyatomic molecules* (1). In general, for more complicated systems Radakovic (56) and Kohlrausch (32) have shown that if the mechanical frequency $\bar{\nu}$ be expressed in wave numbers per centimeter, and the mass in relative atomic weights, and if $n^2 = 5.87 \times 10^{-2} \cdot \bar{\nu}^2$ (cf. equation 5) is introduced as an abbreviation, then the characteristic determinant whose roots give the normal vibrations is for the general case

$$n^6 - an^4 + bn^2 - \bar{c} = 0 \quad (7)$$

$$\left. \begin{aligned} a &\equiv n_1^2 + n_2^2 + n_3^2 = \frac{F_0}{\bar{\mu}_0} + \frac{F_1}{\bar{\mu}_1} + \frac{F_2}{\bar{\mu}_2} \\ b &\equiv n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2 = \frac{F_0 F_1}{\bar{\mu}_0 \bar{\mu}_1} + \frac{F_1 F_2}{\bar{\mu}_1 \bar{\mu}_2} + \frac{F_0 F_2}{\bar{\mu}_0 \bar{\mu}_2} - \frac{F_0 F_2}{m_0^2} \cos^2 \alpha_0 - \frac{F_1 F_0}{m_1^2} \cos^2 \alpha_1 - \frac{F_2 F_1}{m_2^2} \cos^2 \alpha_2 \\ \bar{c} &\equiv n_1^2 n_2^2 n_3^2 = F_0 F_1 F_2 \left[\frac{1}{\bar{\mu}_0 \bar{\mu}_1 \bar{\mu}_2} - \frac{\cos^2 \alpha_2}{m_2^2 \bar{\mu}_0} - \frac{\cos^2 \alpha_1}{m_1^2 \bar{\mu}_2} - \frac{\cos^2 \alpha_0}{m_0^2 \bar{\mu}_1} + \frac{2 \cos \alpha_0 \cos \alpha_1 \cos \alpha_2}{m_0 m_1 m_2} \right] \end{aligned} \right\} (8)$$

where m_0 , m_1 , and m_2 are the relative masses, and F_0 , F_1 , and F_2 the binding forces and α_0 , α_1 , and α_2 the valence angles as indicated in figure 3.

The general case described in equation 7 cannot be immediately applied. However, in simplified cases with molecules of more or less high degree of symmetry a practical application may be made.

(2) *Triatomic molecules*. With molecules of type AX_2 there are

two possibilities: if the molecule is linear there exist a symmetrical oscillation, as shown in II (A, figure 4), an asymmetric oscillation, as shown in I, and a deformation oscillation, as shown in III. If the molecule is non-linear, of type AX_2 , the oscillations are indicated by B. This leads to three equations relating the

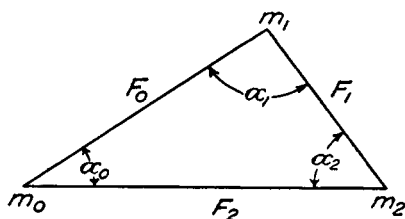


FIG. 3. DISTRIBUTION OF FORCES AND MASSES IN A POLYATOMIC MOLECULE

The masses are represented by m , the interatomic forces by F , and the valence angles by α

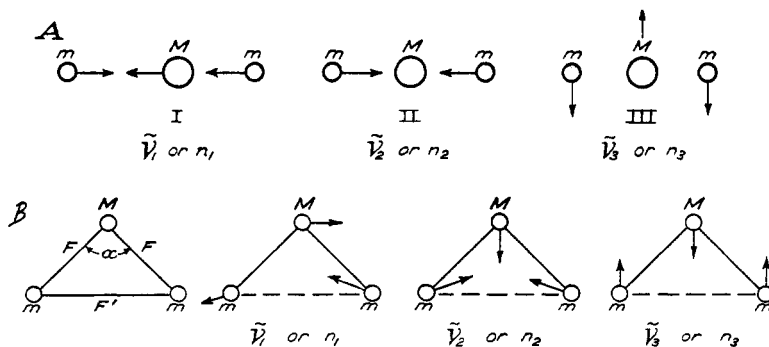


FIG. 4. POSSIBLE TYPES OF OSCILLATION IN LINEAR AND NON-LINEAR MOLECULES OF TYPE AX_2

A represents the type of motion in a linear model and B the motion in a non-linear model.

mechanical frequencies to the restoring force and the respective masses for the linear model:

$$\left. \begin{aligned} n_2 &= \sqrt{\frac{F}{m}} & (a) \\ n_1 &= \sqrt{F \times \frac{M+2m}{Mm}} & (b) \\ n_3 &= \sqrt{d \times \frac{M+2m}{Mm}} & (c) \end{aligned} \right\} \quad (9)$$

Hence the ratio of n_1 and n_2 is given by

$$\frac{n_1}{n_2} = \sqrt{\frac{M+2m}{M}} \quad (10)$$

We shall see presently how this relationship may fit specific examples. n_2 is a symmetrical vibration and will be the most intense.

In molecules of the type X_3 (which is a special case of type AX_2) spacially arranged in the form of an equilateral triangle and in which the masses and binding forces are equal, i.e., when

$$m_0 = m_1 = m_2 = m; \quad F_0 = F_1 = F_2 = F; \quad \alpha_0 = \alpha_1 = \alpha_2 = 60^\circ$$

then equation 8 reduces to

$$\left(n^2 - 3\frac{F}{m}\right)\left(n^2 - \frac{3F}{2m}\right)^2 = 0. \quad (11)$$

This gives two solutions according to Bhagavantam (14), namely,

$$n_1 = \sqrt{3\frac{F}{m}} \quad \text{and} \quad n_2 = \sqrt{3\frac{F}{2m}}$$

The latter value, being a double root, would split into two different frequencies by a disturbance of the symmetry. The ratio of the frequencies obtained is

$$\frac{n_1}{n_2} = \sqrt{2} \quad (12)$$

With molecules of the type AX_2 in which two light atoms are bound to the central atom with equal binding force, in the form of an isosceles triangle, the following relations are obtained, referring to B, figure 4, and comparing this with figure 3. Here one may consider

$$\begin{array}{ll} m_0 = M & \alpha_0 = \alpha \\ m_1 = m_2 = m & \alpha_1 = \alpha_2 = 90^\circ - \frac{\alpha}{2} \\ F_0 = F_2 = F & \\ F_1 = F' & p = \frac{M+2m}{M} \end{array}$$

From the considerations of Dennison (26) and Bjerrum (17) the following three equations are obtained relating the frequencies of vibration with the valence angles and the respective masses:

$$n_1^2 = \frac{F}{m} \left[p + (1-p) \cos^2 \frac{\alpha}{2} \right] \quad (13a)$$

$$n_2^2 n_3^2 = 2 \frac{F'}{m} \cdot \frac{F}{m} \left[p \cos^2 \frac{\alpha}{2} \right] \quad (13b)$$

$$n_2^2 + n_3^2 = 2 \frac{F'}{m} + \frac{F}{m} \left[1 - (1-p) \cos^2 \frac{\alpha}{2} \right] \quad (13c)$$

If there are no criteria for the magnitude of the valence angle, α , this can be approximated by comparing the experimental

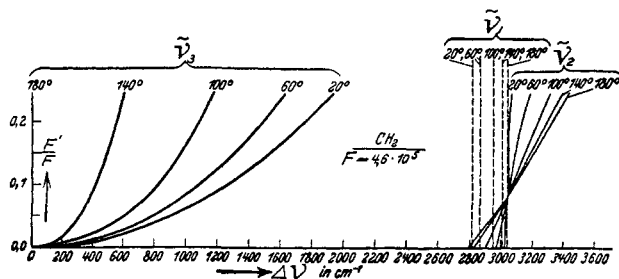


FIG. 5. POSSIBLE RAMAN FREQUENCY SHIFTS AS A FUNCTION OF VALENCE ANGLE AND RESTORING FORCES
(After Kohlrausch, "Der Smekal-Raman-Effekt")

frequencies with the three theoretical frequencies. The form of vibration belonging to n_1 must be so constituted that the distance from m to m is not altered by it. This vibration results in a displacement of the electrical center of gravity and is in consequence optically active. The relative vibrations as a function of the ratios of $F':F$ and the valence angles are given in figure 5.

Where Kohlrausch (33) gives these relations for the group CH_2 , assuming a force constant of 4.6×10^5 dynes per centimeter, it is obvious, for example, that for $\alpha = 180^\circ$, $\bar{\nu}_3$ becomes 0, that $\bar{\nu}_1$ is independent of $\frac{F'}{F}$ and increases with increased α , while $\bar{\nu}_2$ decreases with increased α in cases of small values of $\frac{F'}{F}$.

In the case of the "valence force system," (34, 42, 57, 75), where the nature of F' is considered more in the light of a deformation force (d), n_1 is identical with equation 13a, but

$$n_2^2 n_3^2 = \frac{F}{m} \cdot \frac{d}{m} \cdot p$$

$$n_2^2 + n_3^2 = \frac{d}{m} \left[p + (1-p) \cos^2 \frac{\alpha}{2} \right] + \frac{F}{m} \left[1 - (1-p) \cos^2 \frac{\alpha}{2} \right] \quad (14)$$

If the quantity $\frac{m^2}{M(M+2m)}$ is small compared to 1,

$$n_1^2 = \frac{F}{m} \left[p + (1-p) \cos^2 \frac{\alpha}{2} \right]; \quad n_2^2 = \frac{F}{m} \left[1 - (1-p) \cos^2 \frac{\alpha}{2} \right];$$

$$n_3^2 = \frac{d}{m} \left[p + (1-p) \cos^2 \frac{\alpha}{2} \right]. \quad (15)$$

(3) Tetratomic and other molecules. For molecules of the type X_4 , phosphorus, for example, Bhagavantam (14) deduces that the frequencies should be expressed by

$$n_1 = \sqrt{\frac{F}{m}}; \quad n_2 = \sqrt{\frac{2F}{m}}; \quad n_3 = \sqrt{\frac{4F}{m}} \quad (16)$$

their ratio being $1:\sqrt{2}:2$. This assumes a tetrahedral model. For a quadrilateral model there are four independent modes of oscillation. For molecules of the type AX_3 there are four frequencies. The atoms in this model are at the apices of a pyramid, although in special cases the atom A may be in the plane of the X atoms. Molecules of the type AX_4 also have four normal frequencies and this model is likewise a tetrahedron. In the vibration associated with n_1 , it is supposed that the tetrahedron expands or contracts symmetrically, the central atom remaining fixed at the center of gravity. The third frequency is attributed to the motion of the central atom vibrating about its mean position within the tetrahedron.

(4) Summary. The foregoing discussion has summarized the treatment of simple molecular configurations and the atomic oscillations as a mechanical problem. This has been based on the

“central force system,” “valence force system,” and Dennison’s system, the essential difference between them being the directions in which the forces act and the magnitude of the forces in the equilibrium state. In complicated molecules, the complete quantitative determination of the mechanical vibration frequencies (and consequently the vibrational Raman spectra which would correspond to these oscillations) is practically an impossibility. Nevertheless, qualitative information as to the mode of possible vibrations, and the molecular configuration to which these owe their origin, is of a distinct utility in the allocation of different Raman lines. Furthermore, as a first approximation, a fairly complicated molecule can be considered as made up of *group units*, and the binding force determined from relatively simple equations. The equations particularly applicable to the elucidation of structural relationships, given herein, are equations 4, 9, 10, 12, 15, and 16.

For the sake of clarity, specific examples may be mentioned: The three observed Raman frequencies for carbon dioxide expected for a linear model are $\Delta\bar{\nu}$ 2350, 1330, and 680; for carbon disulfide, $\Delta\bar{\nu}$ 1470, 655, and 745, corresponding to $\Delta\bar{\nu}_1$, $\Delta\bar{\nu}_2$, and $\Delta\bar{\nu}_3$, respectively. According to equation 10,

$$\frac{\Delta\bar{\nu}_1}{\Delta\bar{\nu}_2} = \sqrt{\frac{M+2m}{M}}$$

or, for example, with carbon dioxide,

$$1.77 = \frac{2350}{1330} \cong \sqrt{\frac{12+32}{12}} = 1.91$$

Or for carbon dioxide the ratio $\frac{\Delta\bar{\nu}_1}{\Delta\bar{\nu}_2}$ observed is 1.77; calculated from equation 10, 1.91. For carbon disulfide this is 2.24 (observed) and 2.51 (calculated).

Applying equation 4 to group oscillations of a series of alcohols, Trumpy (69) obtained the following:

| | $\Delta\bar{\nu}$ <i>Observed</i> | $\Delta\bar{\nu}$ <i>Calculated</i> |
|--|--------------------------------------|--|
| (CH ₃)—(OH)..... | 1040 | 1055 |
| (C ₂ H ₅)—(OH)..... | 890 | 910 |
| (C ₃ H ₇)—(OH)..... | 857 | 855 |
| (C ₄ H ₉)—(OH)..... | 823 | 823 |

Calculations of the valence angle, α , in non-linear simple triatomic molecules can be made approximately from the following:

$$\frac{n_1}{n_2} = \sqrt{\frac{M + 2m \sin^2 \alpha}{M + 2m \cos^2 \alpha}} \quad (17)$$

which is based on previously given considerations. This leads to the following values of α for the compounds listed:

| | α |
|-------------|----------|
| O=C=O | 180° |
| S=C=S | 180° |
| H-S-H | 90° |
| O=S=O | 120° |

The application of equation 4 to calculate the binding force to specific types of chemical linkage is obtained from the Raman spectra examination of simple substances which contain either

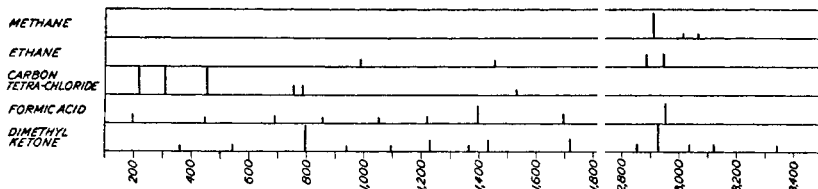


FIG. 6. CHARACTERISTIC RAMAN FREQUENCY SHIFTS AS A FUNCTION OF CHEMICAL CONSTITUTION

this linkage alone, as in the case of diatomic molecules, or by attributing a specific Raman frequency to a type of binding by empirical but nevertheless logical means. This is accomplished in the following manner: In figure 6 are given the Raman frequency shifts for several organic compounds.

It is apparent in the case of methane that the only linear harmonic oscillation possible is that of hydrogen against carbon (the two highest-frequency weak lines are doubtful). The shift at $\Delta\bar{\nu}$ 2915 is therefore attributed to the carbon-hydrogen oscillation. This is substantiated by the fact that carbon tetrachloride, which contains no hydrogen, has no Raman shifts in this region. In the case of ethane, where there is both a possibility of carbon-to-carbon and carbon-to-hydrogen oscillations,

the appearance of a line at $\Delta\bar{\nu}$ 999 is obviously indicative of the carbon-to-carbon oscillation. This does not *a priori* exclude $\Delta\bar{\nu}$ 1460, but from other considerations which will not be discussed at this time, $\Delta\bar{\nu}$ 1460 has been found to be due to the deformation oscillation of the H—C linkage. Ethane has more than one linear harmonic carbon-to-hydrogen oscillation. In the case of the acid and the ketone the $\Delta\bar{\nu}$ 1647 and 1712, respectively, are correctly attributable to C=O, since these lines only appear in this region in compounds containing such linkages. From these and similar considerations with other compounds, both organic and inorganic, one is able to estimate the restoring force exerted by the atoms in the normal state. In the case of ques-

TABLE I
Valence forces (F)

| LINKAGE | $F \times 10^{-5}$ DYNES CM. ⁻¹ | LINKAGE | $F \times 10^{-5}$ DYNES CM. ⁻¹ |
|---------|--|---------|--|
| C—H | 5.02 | C—C | 4.40 |
| N—H | 6.39 | C—N | 4.53 |
| O—H | 6.72 | C—O | 5.05 |
| Cl—H | 4.38 | H—H | 5.38 |
| C=C | 11.0 | C≡C | 14.82 |
| C=O | 11.7 | C≡N | 19.23 |
| O=O | 11.4 | C≡O | 18.83 |
| | | N≡N | 22.30 |

tions of disputed structures, a more careful analysis is necessary, and the identification of other frequency lines corresponding to the probable oscillation frequencies of a given molecular configuration is essential. In table I are given some types of atomic linkages and their corresponding restoring forces.

This leads to the conclusion that the binding force between the atoms executing a simple harmonic displacement from an equilibrium position does not depart far from 5×10^{-5} dynes per centimeter as an average value for a single linkage. The departures from this average, however, have significance. It is also equally clear that atoms joined with a double bond are held together with valence forces approximately twice as great as in the case of

the single bond. In the case of triple bonds, the forces exerted by the similar atoms are approximately three times those of the same atoms joined with a single bond. In some cases this force constant is greater than three times the constant for a single bond. This evidence from Raman spectra has, for instance, long indicated the nature of the triply bonded oxygen to carbon in carbon monoxide, a conclusion to which Langmuir came from chemical considerations more than a decade ago, and to which Pauling (53) has recently come from quantum-mechanical considerations.

B. INTENSITIES OF RAMAN LINES

Raman frequency shifts may be completely described only in terms of three coördinates, namely, magnitude of the shifts, their intensities, and their degrees of polarization. It has already been indicated that the magnitudes of the frequency shifts are primarily a function of the type of oscillation and are dependent, therefore, on the binding force and the relative mass of the oscillating components. From a general point of view the intensities of Raman spectra shifts are directly dependent upon the number of molecules present, which may act as emitters. This makes the Raman spectra studies of gases particularly difficult. Apart from this consideration, in general, the intensities of the Raman scattering follow approximately the same laws as are applicable to Rayleigh scattering, that is, they increase proportionately to λ^{-4} . This has recently been confirmed by Werth (74). Ornstein and Rekveld (49) compare the intensities of the Raman scattering from carbon tetrachloride, using mercury lines 5460, 4358, and 4047 A.U. as exciting lines. Similar observations were made with quartz (51). The Rayleigh fourth-power law was found to hold very accurately. This does not hold, however, when the frequency of the exciting line approaches the value

$$\frac{E_n - E_k}{h}$$

where E_n is the energy of the "third level" previously mentioned. Sirkar (63) observed that excitation by the 3132 A.U. mercury

line results in Raman scattering about 1.38 times more intense than would be indicated by the Rayleigh fourth-power law relative to the 4358 line, and further (64) that the Raman lines of large frequency shifts deviate more from the fourth-power law than small shifts. He further postulates that large deviations may be due in part to changes in optical polarizability and anisotropy, these changes being quite different for different exciting lines and different modes of vibration (45, 46).

It has heretofore been pointed out that the relative intensities depend upon the nature and number of the "third levels" with which the initial and final ones in the Raman shifts can combine. The rules applicable to the relative intensities of individual Raman lines have been formulated by Van Vleck (70), the most intense scattering being from the symmetrical or inactive oscillations.

Relative Raman scatterings for individual compounds have been measured by Ellenberger (28), Segré (62), Landsberg and Mandelstam (39), and Weiler (72, 73). Intensities of specific Raman shifts will be further discussed in the consideration of individual compounds.

The vibrational anti-Stokes lines owe their origins to the fact that the molecules which act as their emitters are not in the normal vibrational state, but in a higher vibrational level. Since, at room temperature, the number of molecules in the higher vibrational states is usually small, the intensity of the anti-Stokes lines, as compared to the intensity of the normal shifts of reduced frequency, is usually very weak. Where they can be elicited, however, an estimation can be made of the population of the molecules in the higher vibrational states. Furthermore the increase in this population, as a function of temperature, may also be determined. From quantitative measurements of the relative intensities of the Stokes and anti-Stokes lines, it has been found that their ratio follows approximately as is to be expected from the Boltzmann distribution; that is,

$$n_{\nu_1} = \beta \cdot e^{\frac{-h\nu_1}{kT}}$$

where k is the Boltzmann constant, T the absolute temperature, and $h\nu$, the energy corresponding to the transition.

Ornstein and Rekveld (48, 50), Placzek (54), and Sirkar (65, 66), have suggested a modified formula. According to Sirkar, the ratio of the intensity of the Stokes and anti-Stokes lines is more accurately represented by the expression

$$\left(\frac{\nu + \nu_{mn}}{\nu - \nu_{mn}}\right)^4 \cdot e^{-\left(\frac{h\nu_{mn}}{kT}\right)}$$

(where ν is the incident frequency and $\nu \pm \nu_{mn}$ the modified radiation), as given by Placzek's theory than by the Boltzmann equation alone.

Actual experimental determinations of the relative intensities of the anti-Stokes and Stokes lines extend back as far as the measurements of Krishnan (36). Brickwedde and Peters (18) noted the rapid increase in the anti-Stokes line $\Delta\bar{\nu}$ 476 in quartz in going from -180° to 550°C . The anti-Stokes line $\Delta\bar{\nu}$ 124 increased less rapidly. The approximate validity of the Boltzmann equation has also been demonstrated by Daure (23). The increase in the intensity of the anti-Stokes lines for calcite with increase in temperature from 150° to 250°C . has been noted by Venkatesachar and Sibaiya (71). Quartz has been similarly examined between 18° and 500°C . by Ney (47), who also noted a slight decrease in the magnitude of the frequency shifts of the anti-Stokes lines, as well as their increased intensities.

C. DEPOLARIZATION OF RAMAN LINES

The degree of depolarization is the third coördinate necessary for a complete description of Raman emissions. It is well-known that general scattering of the Rayleigh type is more or less polarized when viewed in the direction normal to the incident radiation, the degree of polarization, however, depending somewhat on the anisotropic character of the molecule. The ratio of the intensity of the horizontal light vibration (i) to the vertical vibration (I) (which is generally preponderant) gives a measure of the degree of depolarization, that is, $\rho = \frac{i}{I}$ where ρ is the de-

polarization factor. In the phenomenon of diffusion from normal liquids, ρ can attain a value of $6/7$.

The experimental studies of the polarization of Raman rays show that each ray can have a state of polarization independent of the normal diffused scattering and of other Raman rays simultaneously emitted. The value of ρ can vary between 0 and slightly less than 1 in liquids (24).

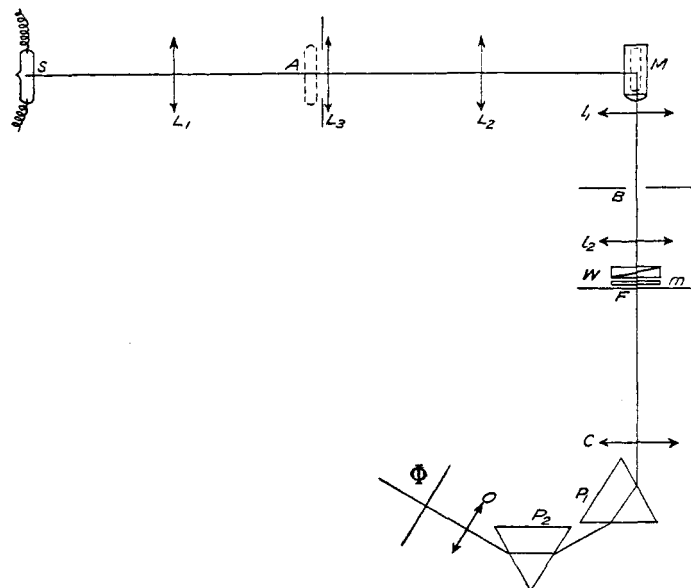


FIG. 7. SCHEMATIC DIAGRAM OF A METHOD USED TO DETERMINE THE DEGREE OF DEPOLARIZATION OF RAMAN LINES
(After Cabannes and Rousset)

Actual experimental measurements of the depolarization are exceedingly difficult, since the experimental arrangement requires the complete elimination of parasitic light. One of the most extensive series of such measurements has been carried out by Cabannes and Rousset (22). The experimental arrangement employed by them is given in figure 7. The image of the exciting source, S, is projected by the lens, L_1 , on a point, A, in front of a rectangular aperture. The lens L_2 reprojects this image so that it is focused in the interior of the Raman tube, M. A third

lens, L_3 , serves a purpose analogous to periscopic collecting lenses. The Raman tube, M , is placed in a vessel containing a liquid having approximately the same index of refraction as the liquid to be studied. A planoconvex lens, of which the center of curvature is in M , is attached to the exit end of the Raman tube. A lens, l_1 , projects the image of the interior of the tube, M , on a rectangular opening, B , and is thence reprojected on the spectroscopic slit, F . The ray diffused at right angles to the incident radiation consists of two incoherent rectangular vibrations, one of which is of maximum intensity, I , perpendicular to the incident ray, and the other is of minimum intensity, i , and parallel to the incident ray. To measure the depolarization factor, ρ , it is necessary to resolve the two diffuse beams. For this purpose a quartz prism, W , is placed before the slit, resulting in two spectral images, one above the other. A mica plate, m , is used to correct the unequal diminution of i and I in traversing the spectrograph prisms. The relative intensities of the two scattered beams may be determined microphotometrically or by other suitable means.

While other observers have used somewhat different experimental arrangements, they are in principle very similar. The description of this apparatus serves to clarify the picture. No brief description, however, can do justice to the care which must necessarily be exercised in carrying out these experiments. It will be pointed out later that some phases of development in Raman spectra depend on the development of the technique employed. In the case of depolarization measurements, this is an example *par excellence*.

According to Cabannes and Rousset, the Raman rays are the result of the interaction of the incident radiation and the fundamental frequency of atomic oscillation in the interior of a molecule. If the atomic nuclei were immovable in their position of stable equilibrium, the refractivity of the molecule and the diffusion of light would be completely defined by a symmetrical force constant (γ), but since this force varies, owing to the nuclei oscillating about their equilibrium positions, it is assumed that the force takes the value of γ_0 . If the normal coördinate which defines the oscillation frequency n or $\bar{\nu}$ be designated by q , the

Raman rays $\bar{\nu}_1 \pm \bar{\nu}_2$ depend upon the derivative of the force $\left(\frac{\partial\gamma}{\partial q}\right)_0$, the same as Rayleigh scattering depends upon the force γ_0 . The symmetrical force γ_0 is connected with two invariants a and b , which are called average refractivity and optical anisotropy. The depolarization factor of Rayleigh scattering by a perfect gas is given in terms of a and b , by the expression:

$$\rho = \frac{6b^2}{45a^2 + 7b^2} \quad (18)$$

The terms "average refractivity" and "optical anisotropy" can also be used in connection with the invariants relative to the force

$$\left(\frac{\partial\gamma}{\partial q}\right)_0$$

and the foregoing formula (equation 18) given for the depolarization factor applied to Raman radiation. There is, however, an essential difference between Rayleigh scattering of a perfect gas and Raman radiation. In the first case the three principal refractivities, of which a is the average, are all positive and the maximum value of ρ cannot exceed 1/2. In the second case the average refractivity can annul itself and ρ attains the value 6/7. The measurement of the depolarization factor in Raman rays permits an estimate of the symmetry and the configuration formed by the atomic nuclei in the interior of the molecule. The molecule in motion does not keep all the elements of symmetry of a molecule at rest, and the oscillations are inactive in *diffusion*, giving the Raman rays of which the depolarization factor is equal to 6/7; that is to say, the ray is depolarized. In order to solve the problem of molecular symmetry of the different possible models for a given molecule, it is necessary to determine *a priori* for each model the number of forbidden rays and the depolarized rays and to compare these results with the experimental determinations.

For example, in the case of sulfur dioxide three characteristic rays, $\Delta\bar{\nu}$ 525, 1146, and 1340, are extant. The values of ρ found for these $\Delta\bar{\nu}$ are, respectively, 0.6, 0.14, and 0.8. The strong ray,

1146, evidently corresponds to a symmetrical oscillation. There remains, then, the question of determining which of the rays $\Delta\bar{\nu}$ 525 and 1340 are provoked by asymmetric oscillation, that is, which gives a depolarization factor equal to 6/7. It is evident from the figures given above that $\Delta\bar{\nu}$ 1340 is the shift which corresponds to the asymmetric oscillation. There are two possibilities in interpreting these data, namely, $\Delta\bar{\nu}_1 = 1340$ and $\Delta\bar{\nu}_2 = 1146$, or $\Delta\bar{\nu}_1 = 1146$ and $\Delta\bar{\nu}_2 = 1340$. The first of these suppositions gives a valence angle for sulfur dioxide corresponding to 118° , the second an angle of 62° . It is evident from the measure of the depolarization that $\Delta\bar{\nu}_1$ is equal to 1340. Hence the calculation of the valence angle,

$$\cos \alpha = \frac{M + m}{m} \cdot \frac{\Delta\bar{\nu}_2^2 - \Delta\bar{\nu}_1^2}{\Delta\bar{\nu}_2^2 + \Delta\bar{\nu}_1^2}$$

gives a value of approximately 119° . In the case of compounds such as water, the most that can be said is that $\Delta\bar{\nu}$ 3240 is depolarized and $\Delta\bar{\nu}$ 3418 polarized. It is necessary to reject, therefore, the hypothesis of Kastler (30) that these two bands are the *P* and *R* branches of the same oscillation. On the basis of these data, α would equal 23° . As will be seen later in a discussion of the Raman spectra of water, the specific assignment of $\Delta\bar{\nu}_1$ or $\Delta\bar{\nu}_2$ to a given Raman frequency is somewhat precarious. In applying polarization considerations to molecules of the type XY_3 , where the nuclei Y may occupy the summits of an equilateral triangle, there are two possibilities, namely, the nucleus X may be on the ternary axis in the same plane as Y, or it may be outside of this plane, in which case the molecule would have a pyramid form. There are four distinct fundamental frequencies, two symmetrical and two degenerate. If the molecule is of pyramidal shape, these four frequencies are active in absorption and diffusion. If the molecule is plane, one of the symmetrical oscillations is inactive in absorption, and the other active in diffusion. The two degenerate frequencies, however, are active in absorption and inactive in diffusion. In the case of phosphorus trichloride, for example, the Raman spectrum is evidenced by four intense rays, indicating a pyramidal construction. From polarization measurements

it is determined that two of these rays are polarized and two depolarized, i.e., $\rho = 6/7$ or 0.857. These are as follows:

Phosphorus trichloride

| | | | | |
|-------------------------|------|------|------|------|
| $\Delta\bar{\nu}$ | 190 | 258 | 484 | 511 |
| ρ | 0.90 | 0.29 | 0.86 | 0.14 |

The molecule is evidently pyramidal in construction. According to this, $\Delta\bar{\nu}$ 190 and $\Delta\bar{\nu}$ 484 are completely depolarized, corresponding to two degenerate frequencies or asymmetrical oscillations, $\Delta\bar{\nu}$ 258 and 511 corresponding to symmetrical oscillations.

TABLE 2

The degree of depolarization of some inorganic compounds

| COMPOUND | ρ | $\Delta\bar{\nu}$ | ρ | $\Delta\bar{\nu}$ | ρ | $\Delta\bar{\nu}$ | ρ | $\Delta\bar{\nu}$ | ρ | $\Delta\bar{\nu}$ | ρ | $\Delta\bar{\nu}$ |
|---------------------------------------|--------|-------------------|--------|-------------------|--------|-------------------|--------|-------------------|--------|-------------------|--------|-------------------|
| CS ₂ | 0.25 | 654 | 0.25 | 799 | | | | | | | | |
| SO ₂ | 0.60 | 525 | 0.14 | 1145 | 0.80 | 1334 | | | | | | |
| PBr ₃ | 0.84 | 116 | 0.18 | 162 | 0.28 | 380 | 6/7 | 400 | | | | |
| PCl ₃ | 0.90 | 190 | 0.29 | 258 | 0.86 | 484 | 0.14 | 511 | | | | |
| AsCl ₃ | 6/7 | 158 | 0.61 | 194 | 6/7 | 370 | 0.08 | 405 | | | | |
| CCl ₄ | 0.83 | 218 | 0.79 | 314 | 0.05 | 458 | 6/7 | 762 | 6/7 | 790 | | |
| SiCl ₄ | 6/7 | 151 | 6/7 | 221 | 0.05 | 425 | 6/7 | 607 | | | | |
| TiCl ₄ | 6/7 | 120 | 6/7 | 144 | 0.05 | 386 | 6/7 | 497 | | | | |
| SnCl ₄ | 6/7 | 105 | 6/7 | 130 | 0.05 | 368 | 0.63 | 403 | | | | |
| POCl ₃ | 0.83 | 193 | 0.64 | 267 | 0.81 | 337 | 0.05 | 486 | 6/7 | 581 | 0.4 | 1290 |
| SO ₂ Cl ₂ | 0.70 | 214 | 0.93 | 280 | 6/7 | 365 | 6/7 | 390 | 0.07 | 408 | 0.06 | 556-563 |
| H ₂ O..... | D | 3240 | P | 3418 | | | | | | | | |

Cabannes and Rousset (22) discuss in detail the application of depolarization measurements to the most general types of molecular configuration. The same principles apply in all cases. The measured depolarization for a number of inorganic compounds is given in table 2.

Bär (12) finds that $\Delta\bar{\nu}$ 1403 for liquid sulfur dioxide is completely unpolarized. Bhagavantam (15) determined the depolarization for carbon tetrachloride, silicon tetrachloride, titanium tetrachloride, and stannic chloride. In no case did the depolarization exceed 6/7. The same conclusion is reached by Bhagavantam and Venkateswaran (16).

Specchia (68) studied the depolarization of water. Cabannes and Rousset (21) concluded that Raman rays resulting from oscillations which do not destroy the symmetry of symmetrical models have a depolarization factor of less than $6/7$. When the symmetry of the molecules is not retained during degenerate oscillations, $\rho = 6/7$, but never exceeds this value. In compounds of the type XCl_4 , all Raman rays have $\rho = 6/7$, except one, whose polarization is due to the periodic contraction of the tetrahedron. Molecules of the type XCl_3 have two degenerate rays where $\rho = 6/7$ and two rays more highly polarized.

Anomalous depolarization in crystals is discussed by Cabannes (20).

The determination of the degree of depolarization of specific Raman frequencies in organic compounds is very useful in the determination of the character of the oscillation to which they owe their origin. This will be reserved, however, for discussion in a later review.

D. THE RAMAN EFFECT AND SPECIFIC HEAT CALCULATIONS

Since the Raman effect investigations have provided a mass of data regarding the fundamental oscillation frequencies of elements and compounds, it is not surprising that attempts have been made to correlate them with specific-heat data for simple substances. This has been done for both organic and inorganic compounds. The discussion contained herein will be limited to some of the inorganic aspects, and the organic aspects reserved for later publication.

Paramasivan (52) considers that the heat capacity per gram molecule for each substance is given by

$$RF_E \left(\frac{\theta}{T} \right) \quad (19)$$

where T = absolute temperature, $\theta = \frac{h}{k} \nu = 4.78 \times 10^{-11} \nu$, and F_E = the Einstein specific-heat function.

In the case of a liquid, the individual molecule possesses three degrees of freedom by virtue of its translational motion and three

degrees of freedom from its rotation. Each degree of freedom has an energy given by

$$RF_D \left(\frac{\theta_m}{T} \right)$$

where F_D is the Debye specific-heat function.

The total heat capacity of a liquid may, therefore, be written in the form:

$$(C)_{\text{mole}} = 6RF_D (\theta_m/T) + \Sigma RF_E (\theta/T) \quad (20)$$

where the summation represents the total Einstein specific-heat functions due to all independent modes of vibration and θ_m represents the average values of $\frac{h\nu}{k}$ for the six degrees of freedom and may be evaluated by the formula of Lindemann (44).

For triatomic gases the linear model has two degrees of rotational freedom and three degrees of translational freedom. Consequently, one obtains

$$(C_{v_r})_{\text{mole}} = 3R + RF_E \left(\frac{\theta_1}{T} \right) + RF_E \left(\frac{\theta_2}{T} \right) + RF_E \left(\frac{\theta_3}{T} \right) \quad (21)$$

for the triangular model, and

$$(C_{v_r})_{\text{mole}} = \frac{5}{2} R + 2RF_E \left(\frac{\theta_1}{T} \right) + RF_E \left(\frac{\theta_2}{T} \right) + RF_E \left(\frac{\theta_3}{T} \right) \quad (22)$$

for the linear model.

Calculations for the specific heats of carbon dioxide, carbon disulfide, and sulfur dioxide, using equations 20, 21, and 22, are given in table 3.

In exceptional cases, in compiling the data used in these tables, where Raman spectra provided only some of the fundamental frequencies, recourse has been had to infra-red absorption data. In the case of multiple structure, the weighted mean is taken as the fundamental frequency, and in the case where a system is degenerate, the degeneracy has been taken into consideration.

For tetratomic molecules, the atoms are in the corners of a pyramid, and each system has six degrees of vibrational freedom.

There are four fundamental frequencies in this system, two of which are double oscillations. The heat capacity in the gaseous state may be expressed as

$$(C_v)_{\text{mole}} = 3R + RF_E \left(\frac{\theta_1}{T} \right) + RF_E \left(\frac{\theta_2}{T} \right) + 2RF_E \left(\frac{\theta_3}{T} \right) + 2RF_E \left(\frac{\theta_4}{T} \right) \quad (23)$$

TABLE 3
Specific heats of triatomic molecules
 $T = 30^\circ\text{C}$.

| COMPOUND | $\Delta\bar{\nu}$ | | | $F_E \left(\frac{\theta}{T} \right)$ | | | $F_D \left(\frac{\theta_m}{T} \right)$ | SPECIFIC HEAT | |
|-------------------------------|-------------------|------|------|---------------------------------------|-------|-------|---|---------------|----------|
| | | | | | | | | Calculated | Observed |
| CS ₂ (liquid)..... | 1470 | 200 | 668 | 0.047 | 0.927 | 0.467 | 0.41 or 0.99 | 0.218 | 0.237 |
| CO ₂ (gas)..... | 2250 | 670 | 1346 | 0.003 | 0.455 | 0.075 | | 0.159 | 0.154 |
| SO ₂ (gas)..... | 606 | 1146 | 1340 | 0.53 | 0.141 | 0.083 | | 0.117 | 0.117 |

TABLE 4
Specific heats of tetratomic molecules

| COMPOUND | $\Delta\bar{\nu}$ | | | | $F_E \left(\frac{\theta}{T} \right)$ | | | | SPECIFIC HEAT | |
|---------------------------------|-------------------|-----|-----|-----|---------------------------------------|-------|-------|-------|---------------|----------|
| | | | | | | | | | Calculated | Observed |
| PCl ₃ (117°C.)..... | 512 | 260 | 488 | 190 | 0.753 | 0.926 | 0.774 | 0.956 | 0.118 | 0.119 |
| AsCl ₃ (217°C.)..... | 410 | 193 | 370 | 159 | 0.887 | 0.971 | 0.907 | 0.981 | 0.095 | 0.098 |

TABLE 5
Specific heats of pentatomic molecules

| COMPOUND | $\Delta\bar{\nu}$ | | | | $F_E \left(\frac{\theta}{T} \right)$ | | | | SPECIFIC HEAT | |
|---------------------------------|-------------------|-----|-----|-----|---------------------------------------|-------|-------|-------|---------------|----------|
| | | | | | | | | | Calculated | Observed |
| SiCl ₄ (97°C.)..... | 221 | 614 | 150 | 424 | 0.937 | 0.647 | 0.969 | 0.804 | 0.123 | 0.117 |
| TiCl ₄ (167°C.)..... | 145 | 494 | 120 | 382 | 0.981 | 0.810 | 0.985 | 0.880 | 0.108 | 0.125 |
| SnCl ₄ (157°C.)..... | 131 | 403 | 106 | 367 | 0.964 | 0.747 | 0.979 | 0.813 | 0.084 | 0.087 |

The calculated values for phosphorus trichloride and arsenic trichloride are given in table 4.

For pentatomic molecules the system possesses nine degrees of freedom and has four fundamental frequencies, some of which

are multiple oscillations due to degeneracy. The specific heat may be calculated from

$$(C_v)_{\text{mole}} = 3R + 3RF_E \left(\frac{\theta_1}{T} \right) + 3RF_E \left(\frac{\theta_2}{T} \right) + 2RF_E \left(\frac{\theta_3}{T} \right) + RF_E \left(\frac{\theta_4}{T} \right) \quad (24)$$

In table 5 are given the values calculated for this equation.

The preceding calculations are of interest but involve a fair number of approximations, and the selection of particular fundamental frequency values has been made somewhat arbitrarily.

SUMMARY

It may be seen from the preceding discussion that Raman spectra investigations have many ramifications. They can provide information as to the possible vibrational and rotational transitions and hence information as to the molecular constitution of the more simple molecules from a purely physical point of view. On the assumption that one may apply with a certain degree of validity the equations relating atomic masses with binding force and frequency, calculations may be made as to the strength of this binding force under normal conditions from experimentally determined frequencies. The amplitude of oscillation of the atomic constituents in a given molecule can be approximated. From the magnitude of the frequency shifts, their relative intensities, their degrees of depolarization, and their number, can be estimated the molecular configuration necessary to fit these coordinates. In the case of debated structure of a given molecular species, this may provide all of the necessary information to distinguish between alternative hypotheses with a high degree of accuracy. It will be evident in the later discussion of the Raman frequency shifts for specific types of compounds how this information can be applied in the elucidation of both known and unknown molecular structures, the composition of liquid mixtures and amorphous solids, and properties of crystals and gases. In short, information valuable to the physicist, the chemist, and the crystallographer is obtainable from such investigations.

III. TECHNIQUE

Since a complete series of Raman lines appears for each exciting or incident radiation, it is highly essential that the incident light be monochromatic. The modified lines or Raman lines are each individually extremely weak as compared to the original source of excitation, so that it is also essential to have great intensities of exciting light and efficient optical systems. It is in this direction—namely, toward monochromatism and adequate intensities—that the major developments in technique have taken place. The most common source of light is the mercury arc; the helium lamps suggested by Wood (103, 104, 105) are more or less impracticable except in special instances. The mercury arc provides three lines of importance, the 4358, 4047, and the 2536 A.U. lines. The use of the 4358 A.U. is quite general, but its utility depends on the elimination of the 4047 A.U. as a simultaneous source of energy.

The failure so to eliminate the 4047 A.U. leads to discordant results which will be discussed later. In addition to these difficulties there is a continuous spectrum from the mercury arc which must be likewise diminished. The standard filter for the removal of the 4047 A.U. line has been an acid solution of quinine sulfate, which, however, has the disadvantage of decomposing on prolonged exposures. Pfund (100) found that a 12-mm. layer of a saturated solution of sodium nitrite shows a 65 per cent transmission of the 4358 A.U. and 1 per cent of the 4047 A.U. lines. Likewise, *m*-dinitrobenzene (81, 90) transmits the greater portion of the 4358 A.U. and little of the 4047 A.U. line. It must be frankly admitted that there is no perfect system and any monochromatic gains are at the sacrifice of some intensity. Krishnamurti (96) has suggested sodium salts of *o*-cresolphthalein for the isolation of the 4047 A.U. mercury line. Corning Red Purple Ultra glass is about as efficacious for this purpose as any filter. For the isolation of the 2536 A.U. mercury line, Bolla (84) used a mercury vapor filter to prevent halation, and Hulubei (92) used chlorine under pressure.

The use of Corning glass Noviol O to eliminate the 3650 A.U. mercury lines, concentrated praseodymium solutions to elimi-

nate some of the halation from the 4358 A.U. mercury line, and a solution of iodine and carbon tetrachloride as a filter to reduce the 4358 A.U. mercury line in favor of the 4047 A.U. mercury line, as well as improved optical arrangements, have been suggested by Wood (106, 107, 108). To increase the intensity of light used for special excitation purposes, lamps other than mercury arcs and especially designed mercury lamps have been employed. Krishnamurti (95) used a cadmium arc (82) containing 50 per cent tin. This gave as exciting lines 4800 A.U., 5086 A.U., and 6438 A.U. A simple capillary fused silica mercury lamp has been described by Daniels and Heidt (87). Lamps similarly constructed but developed to use metals other than mercury, such as bismuth, cadmium, lead, thallium, and zinc, have been constructed by Hoffman and Daniels (91). A special mercury lamp designed with a discharge surrounding the material to be investigated is described by Venkatesachar and Sibaiya (71). This is similar to the lamp previously developed by Bates (102) for photochemical studies. A spiral mercury lamp for the study of crystals has been developed by Hibben (89). A hot cathode helium lamp in a reflecting apparatus so arranged that the Raman tube is at one of the foci of the ellipse, the helium lamp at the other, has been described by Buttolph (86).

To accomplish much greater increases in effective intensity, more efficient optical systems are necessary. They have been discussed by Anand (79, 80), Almasy (78), Grassmann (88), and Mesnage (98). The filling up of the spectrogram with light has been considered as a geometrical problem by Nielsen (99). Other improvements have been suggested by Hulubei and Cauchois (93, 94) and by Ziemecki (109).

A rapid spectrograph of high dispersion for Raman effect studies in the visible region of the spectrum has been designed by Bourguel (85).

A special apparatus for studying the Raman effect in liquids at liquid air temperatures has been described by McLennan, Smith and Wilhelm (97).

Typical apparatus used for the investigation of the Raman effect of gases under pressure has been designed by Bhagavantam (83) and Rasetti (101).

Development in technique of Raman effect applications has been relatively slow. This is partially because some results are obtainable under almost any circumstances. The importance of further necessary improvements cannot be overestimated. The scope and the accuracy of future observations are in a large measure dependent on the refinements in procedure already developed and in the continued improvement of the experimental method.

IV. RAMAN SPECTRA OF INORGANIC CRYSTALS

The Raman effect in inorganic crystals serves the purpose of determining the Raman shifts for compounds whose structures and compositions are sometimes known since there are three other independent sources of information concerning them, namely, analytical, crystallographic, and x-ray. With a partially identified constitution, therefore, the Raman lines obtained from such investigations can be attributed with some degree of certainty to definite interatomic oscillations and configurations. This is a mandatory preliminary for the study of the Raman effect in solutions. If the Raman lines given by a group are determined in the crystalline form and the same lines persist when the crystal is dissolved, then it is not unreasonable to suppose that the same group or groups persist in solution. For example, if the Raman lines of a series of nitrites are determined in crystalline form and the same lines persist in the aqueous solution of these substances, this is *a priori* evidence that the nitrite exists *as such* in solution. Conversely, variations from these determinations are *a priori* evidence that modification of the solute in solution exists. This application will be discussed further in the consideration of the Raman effect of acids, alkali solutions, and intermediate compounds. The interpretation of the Raman effect in amorphous solids is likewise predicated upon a similar phenomenon.

Large numbers of crystals were examined prior to 1931. It would serve no useful purpose to repeat many of these. There are some, however, somewhat out of the ordinary, which might be advantageously mentioned.

*Chlorates, bromates, iodates, tungstates, molybdates, perchlorates,
and periodates*

Krishnamurti (134) found for NaClO_3 , KClO_3 , $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, NaBrO_3 , KBrO_3 , KIO_3 , HIO_3 , $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, NH_4ClO_4 , KIO_4 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, PbMoO_4 , CaWO_4 , and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ the principal Raman shift $\Delta\bar{\nu}$ 930 of the chlorates to be represented by two shifts 770 and 842 in the bromates and by four, 733, 751, 784, and 801 in the iodates. The perchlorates give Raman lines at 462, 633, and 933. The molybdates give shifts of 932 and 880; the tungstate 928.

For crystalline sodium bromate Schaefer, Matossi, and Aderhold (156) observed $\Delta\bar{\nu}$ 357, 370, 799, and 836, $\Delta\bar{\nu}$ 799 being very strong, and for cadmium bromate $\Delta\bar{\nu}$ 787.

Sulfates

The frequency shifts for fifteen crystalline inorganic sulfates were determined by Krishnamurti (133). These comprised iron, nickel, ammonium, zinc, copper, potassium, magnesium, mercury, barium, manganese, sodium, strontium, cadmium, calcium sulfates, and potassium alum. The magnitude of the shifts depends somewhat on the cation. On the average they correspond to $\Delta\bar{\nu}$ 454, 625, 990, and 1120. Not all of these frequencies were found, however, for each element examined.

More recently, Nisi (146) determined the Raman spectra of the sulfate crystals of lithium, sodium, potassium, rubidium, ammonium, beryllium, magnesium, zinc, cadmium, calcium, barium, strontium, copper, nickel, iron, manganese, potassium alum, ammonium iron sulfate, and sodium thiosulfate. On the average the $\Delta\bar{\nu}$ obtained from these crystals were 415, 462, 619, 986, 1006, 1076, and 1125. Of these shifts those near $\Delta\bar{\nu}$ 1000 were strong, and $\Delta\bar{\nu}$ 462 and 671 diffuse and of medium or less intensity. Copper sulfate showed a number of lines between $\Delta\bar{\nu}$ 84 and $\Delta\bar{\nu}$ 280.

Sodium thiosulfate pentahydrate gave $\Delta\bar{\nu}$ 324, 434, 546, 612, 674, 1018, 1116, 1163. Of these $\Delta\bar{\nu}$ 434 was classed as very strong and $\Delta\bar{\nu}$ 1018 medium.

The spectrum of the deformed sulfate ion is compared with that

of a regular tetrahedron by Cabannes (113), who obtained for calcium sulfate dihydrate (gypsum) $\Delta\bar{\nu}$ 414, 495, 620, 671, 1109, and 1133. The shift $\Delta\bar{\nu}$ 671 is anti-symmetrical to the binary axis L . Gypsum and barite (BaSO_4) were also investigated by Rasetti (153). Hollaender and Williams (127) obtained $\Delta\bar{\nu}$ 696, 980, and 1128 from gypsum and $\Delta\bar{\nu}$ 461, 702, and 980 from barite.

Nitrates

The nitrates have been studied extensively. Menzies (142) obtained $\Delta\bar{\nu}$ 1052 for potassium nitrate, using coarse crystals. Bär (110) obtained the Raman spectra of sodium, ammonium, and calcium nitrates. Ammonium nitrate gave $\Delta\bar{\nu}$ of 706 and 1056; calcium nitrate, 1054; and sodium nitrate, 1074.

Krishnamurti (135, 130, 137) investigated some eighteen nitrates. The strongest line identified as the inactive frequency of the nitrate ion (116) varies from 1030 to 1066, depending upon the cation. Other lines were present for the nitrates of the alkalis and some of the alkaline earths. On an average, these were $\Delta\bar{\nu}$ 185, 725, 1380.

Nisi (148) examined single crystals of sodium nitrate and obtained $\Delta\bar{\nu}$ 101, 189, 723, 1067, 1385, and 1666. Under like conditions he obtained the following results: For potassium nitrate, $\Delta\bar{\nu}$ 31, 51, 84, 711, 1048, and 1344; for rubidium nitrate, $\Delta\bar{\nu}$ 109, 147, 705, 1056, and 1364; for cesium nitrate, $\Delta\bar{\nu}$ 116, 149 (?), 715, 1050, and 1346; and for ammonium nitrate $\Delta\bar{\nu}$ 59, 86, 142, 170, 714, 1041, 1869.

Single crystals of sodium nitrate, crystallized from the molten solution, give $\Delta\bar{\nu}$ 103, 190, 730, 1074, 1391, and 1678. The first two of these were considered by Cabannes and Canals (114) as external frequencies, the succeeding three as fundamental frequencies, and $\Delta\bar{\nu}$ 1678 as a combination frequency. Of these fundamentals, $\Delta\bar{\nu}$ 730 and 1391 are active and $\Delta\bar{\nu}$ 1074 inactive.

Nitrites

For sodium nitrite, Carrelli, Pringsheim and Rosen (116) obtained $\Delta\bar{\nu}$ 696, 785, 1303. Bär (110) obtained $\Delta\bar{\nu}$ 1333.

Halogen compounds

Crystalline inorganic chlorides containing more than one atom in the anion have been investigated by Krishnamurti (131) and the following $\Delta\bar{\nu}$ were obtained: HgCl_2 , 313, 381; Hg_2Cl_2 , 165, 273, 295, 320; ZnCl_2 , 234; CdI_2 , 105, 345, 395; SbCl_3 , 145, 166, 312, 337; BiCl_3 , 153, 169, 242, 288; PCl_5 , 248, 356, 405, 450.

Krishnamurti (136) found that the Raman spectrum of mercuric chloride gives a strong line at $\Delta\bar{\nu}$ 313 and a fainter at 381, whereas mercuric bromide gives only one at $\Delta\bar{\nu}$ 187.

The Raman spectrum of sodium chloride has been sought by Fermi (118) and by Fermi and Rasetti (119). The effect in this case is extremely weak and is considered a Raman effect of the second order.

Haun and Harkins (123) found germanium tetrachloride to yield Raman lines at $\Delta\bar{\nu}$ 132, 171, 397, and 451. The first two are optically active and the other two inactive.

The Raman spectra of aluminum chloride $\Delta\bar{\nu}$ 541 and 806 (125), sodium silicate, orthophosphoric acid, and potassium hydrogen phosphite were determined by Hibben (124).

The Raman spectra of fluorite, anhydrite, rock salt, and ice have been investigated by Rasetti (152, 153), using the 2536 A.U. line of mercury as the primary radiation. New bands were observed. The Raman effects of molecules of XY_6 and XY_5 , such as HSbCl_6 and H_2SnCl_6 and SbCl_5 were investigated by Redlich (154).

The large frequency shifts of $\Delta\bar{\nu}$ 7256 and 7270, respectively, found by Rasetti (151) in fluorite and calcite have been attributed by Tomaschek (157) to the phosphorescent lines of gadolinium, known to be present in natural fluorite.

Silicates and phosphates

The fundamental frequencies of the SiO_4 group in quartz crystals have been determined by Weiler (158). These are $\Delta\bar{\nu}$ 502, 800, 1062–1086, 1170–1208. With the aid of these, the entire infra-red spectrum below 10μ can be interpreted as a system of combination bands of the second to the fourth order. A study

was also made of polymeric homologous series of silica esters (159, 160). In these compounds four characteristic scattered frequencies must be attributed to SiO_4 .

The average shifts obtained from quartz, SiO_2 , were $\Delta\bar{\nu}$ (85),¹ (106), 127, 207, 267, (321), 355, 404, 465, 702, (740), 802, 1070, (1111), 1164, 1227. The investigation of quartz has been conducted by Landsberg and Mandelstam (37, 140, 141), Hollaender and Williams (126, 127), Gross and Romanova (122), Pringsheim and Rosen (149), Wood (161), Menzies (143), Daure (24), Ney (47), Krishnan (138, 139), Nisi (144, 145), Rao (150), Brickwedde and Peters (18), and Rasetti (153). Of the shifts given $\Delta\bar{\nu}$ 127 and $\Delta\bar{\nu}$ 465 are strong.

The Raman effect in phosphates and silicates was investigated by Nisi (147). The Raman spectra of apatite, beryllonite, phenacite, topaz, beryl, danburite, zircon, and tourmaline were examined in detail. The following $\Delta\bar{\nu}$ were observed: For apatite, $\text{Ca}_5(\text{F}, \text{Cl})(\text{PO}_4)_3$, $\Delta\bar{\nu}$ 442, 592, 966, and 1044 ($\Delta\bar{\nu}$ 966 strong); for beryllonite, BeNaPO_4 , $\Delta\bar{\nu}$ 232, 354, 416, 463, 572, 612, 1010, 1045, and 1070 ($\Delta\bar{\nu}$ 1010 strong); for phenacite, Be_2SiO_4 , $\Delta\bar{\nu}$ 219, 378, 444, 523, 876, 915, 947, 1014 ($\Delta\bar{\nu}$ 876 strong); for topaz, $\text{Al}(\text{F}, \text{OH})_2\text{SiO}_4$, illuminated parallel to the $z(y)$ axis, $\Delta\bar{\nu}$ 243, 270, 288, 336, 393, 520, 560, 857, 925, 983, 1007, 1165, (3649) ($\Delta\bar{\nu}$ 925, 270 strong); for beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, $\Delta\bar{\nu}$ 318, 393, 424, 450, 528, 624, 684, 1012, 1074, 1243, 1390, 1519, (3607) ($\Delta\bar{\nu}$ 684 strong); for danburite, $\text{CaB}_2\text{Si}_2\text{O}_8$, $\Delta\bar{\nu}$ 92, 124, 186, 207, 242, 269, 289, 342, 371, 422, 608, 884, 970, 1110, 1158, 1205 ($\Delta\bar{\nu}$ 608 strong); for zircon, ZrSiO_4 , $\Delta\bar{\nu}$ 355, 438, 1006 ($\Delta\bar{\nu}$ 1006 strong); for olivine, Mg_2SiO_4 , $\Delta\bar{\nu}$ 146, 827, 856 (all doubtful). For topaz the intensity of the Raman lines is a function of the direction of observation and illumination.

Krishnan (139) observed $\Delta\bar{\nu}$ 1053 for topaz.

Carbonates

Magnesite (MgCO_3) gives $\Delta\bar{\nu}$ 1098, and cerussite (PbCO_3) $\Delta\bar{\nu}$ 59, 74, 102, 118, 146, 177, 1052, 1363, and 1476 as observed by

¹A wave number shift in parentheses indicates some doubt as to its numerical value or as to its existence.

Schaefer, Matossi, and Aderhold (156). In the latter compound the two lowest frequencies, as well as $\Delta\bar{\nu}$ 1052, are strong.

Aragonite (CaCO_3) has been investigated by Kimura and Uchida (128, 129), Schaefer, Matossi, and Aderhold (156), Bhagavantam (112), Nisi (148), and Rasetti (153), who obtained $\Delta\bar{\nu}$ 94, 156, 209, 271, 708, and 1087 for average values.

Calcite (CaCO_3) has been extensively investigated by Landsberg and Mandelstam (37, 140, 141), Wood (161), Kimura and Uchida (129), Krishnan (139), Nisi (144), Schaefer, Matossi, and Aderhold (155, 156), Daure (24), Embirikos (117), Venkatesachar and Sibaiya (71), Bhagavantam (112), Rasetti (151), Cabannes and Canals (114), Cabannes and Osborne (115), and Rasetti (153). On the average the following $\Delta\bar{\nu}$ were obtained: 132, (147), 155, (161, 221), 282, 714, (771, 877), 1088, (1438), (1747), (7270, 7345, 7395, 7456). The frequency shifts indicated in parentheses are doubtful, particularly the four large frequency shifts.

Hydroxides

Krishnamurti (96) found that crystalline sodium hydroxide gives a strong sharp line at $\Delta\bar{\nu}$ 3630, which is attributed to the OH ion.

Sulfur and phosphorus

Irradiating sulfur crystals at liquid air temperatures, Krishnamurti (136) has obtained four Raman lines corresponding to $\Delta\bar{\nu}$ 151, 218, 447, 475, all of which are strong except $\Delta\bar{\nu}$ 447.

Three Raman shifts are obtained from yellow phosphorus, $\Delta\bar{\nu}$ 374, 468, and 607 (111).

The Raman effect of crystals of PH_4I has been studied by Gopal Pai (121), with a view to correlating it with the crystal structure of the compound. The $\Delta\bar{\nu}$ found are 930, 1040, 1130, 1259, 1416, 2304, 2370. All these frequencies were attributed to the ionic group PH_4 .

SUMMARY

Some of the material in the foregoing has been included not only because of its intrinsic interest but also as a matter of reference standard for the discussion on solutions.

No attempt has been made to indicate, except in a general manner, the relative intensities, regardless of the fact that intensity is one of the factors necessary to the full description of a Raman shift. This is for two reasons: in practically no case has the intensity been measured by microphotometric means; and the halation due to general scattering makes visual estimates only very roughly approximate. Very marked differences in intensity are, however, easily discernible.

The crystalline compounds examined comprise most of the more common types of inorganic salts. In a given type group, there are some regular differences which are reasonably noticeable. It should be borne in mind, however, that generally a difference of a few wave numbers may be well within the experimental error in measuring the magnitude of the displacement. Measurements by different observers will often produce a difference in estimating the maximum of a few wave numbers.

As pointed out by Krishnamurti, the displacement of the strongest line characteristic of the SO_4 group near $\Delta\bar{\nu}$ 1000 is a function of the cation, decreasing with increasing volume of the cation, e.g., $\Delta\bar{\nu}$ for sodium 995, potassium 981, ammonium 974. This depends, however, upon the particular group of the periodic system in which a given series lies. For calcium the shift is $\Delta\bar{\nu}$ 1008, strontium 999, and barium 988.

In the tetrahedron model suggested for the SO_4 group, the $\Delta\bar{\nu}$ 1120 and 625 are taken as active frequencies and $\Delta\bar{\nu}$ 990 and 454 are inactive ones. The SO_4 group may be easily deformable, as is evidenced by the variable nature of the positions and intensities of the lines (133), and it may therefore depart, to a considerable extent, from a tetrahedral symmetry.

Another striking fact which emerges from this investigation is that this shift ($\Delta\bar{\nu}$ 990) is very much weakened in substances which have a large paramagnetic susceptibility, in this case iron, nickel, copper, and manganese. All diamagnetic sulfates show this line prominently.

Nisi (146) takes exception, however, to this observation regarding paramagnetic crystals. He obtained for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ a line of medium intensity at $\Delta\bar{\nu}$ 984 and a faint one at 1096. For

$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ two lines were observed, $\Delta\bar{\nu}$ 994 and 1087, and for $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, one line at 985. In addition to this he observed that the more complicated sulfates, such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, tend to have more complicated Raman spectra, the lines corresponding to active vibrations splitting into doublets or triplets, the higher frequency shift component being the more intense. In the series lithium, sodium, potassium, rubidium and ammonium sulfates the frequency shift of the inactive line near $\Delta\bar{\nu}$ 1000 decreased as the cation volume increased. The spectrum obtained from gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) showed considerable variation in the intensity of this line ($\Delta\bar{\nu}$ 1000) depending upon the direction of illumination and observation. Roughly speaking, in the cases of illuminations from the direction parallel to the $b(y)$ axis and observed from various directions, the intensity of one component of the doublet $\Delta\bar{\nu}$ 415 and 493 reaches a maximum and that of the other a minimum, and *vice versa*, when these two directions are nearly perpendicular to each other.

The strongest line for the nitrates, as previously mentioned, is that which corresponds to the inactive frequency of the nitrate ion. According to Krishnamurti (130), the latter corresponds to a symmetrical vibration of the three oxygen atoms toward and away from the central atom, producing no change in electrical moment. The oxygen atoms occupy the corners of a plane equilateral triangle with the nitrogen atom at the center. The vibration corresponding to $\Delta\bar{\nu}$ 725 is due to the movement of any one oxygen atom along the median followed by a small alternate elongation and diminution of the opposite side of the group (this may also be considered a drum-head vibration of the ion, the nitrogen atom vibrating perpendicularly to the plane), while the shift at $\Delta\bar{\nu}$ 1380 is due to the oscillation of the nitrogen atom along or perpendicular to any median. As in the case of the sulfates, there is a slowing down of the oscillation frequency with the increase in atomic weight of the metal ion (120). It was observed that lithium, sodium, and magnesium nitrates showed a fairly large frequency shift (maximum value $\Delta\bar{\nu}$ 1069), while calcium, barium, lead, potassium, aluminum, cadmium, and silver showed intermediate values, the smaller shifts (minimum value $\Delta\bar{\nu}$ 1037)

being exhibited by lead, mercury, and bismuth. The view was put forth that, in the fully ionized crystals, the influence of the cation on the vibration of the anion is proportional to the volume occupied by the cation in the crystal lattice, although in this case this is disputed by Nisi (148). The smaller the volume, the greater the characteristic oscillation frequencies associated with the nitrate group.

Only two out of the three active frequencies of the nitrates recorded by infra-red measurements appear as Raman lines. One of these is, on the average, $\Delta\bar{\nu}$ 725. For the alkali metals this shift also decreases with increased volume of the cation. But with barium and lead nitrates a too large frequency shift was observed. It was concluded that the frequency observed with the alkali nitrates is different in origin from those observed with strontium, barium, and lead nitrates. With the former compounds, it was postulated that the vibrations are in the plane of the NO_3 group, while with the latter the $\Delta\bar{\nu}$ probably represent vibrations of the nitrogen atom at right angles to the plane. This explanation is a matter of opinion.

The second active frequency, $\Delta\bar{\nu}$ 1380, is more a broad band with the higher nitrates than with lithium and sodium, for example. The actual maximum changes little. The lowest frequency shift, $\Delta\bar{\nu}$ 185 (on the average), varies considerably from compound to compound. Krishnamurti attributes this to a lattice vibration probably involving mutual swings between the nitrate ion and the cation. Its frequency is greater for a smaller cation. This vibration disappears in solution.

The halides may be classified, according to Krishnamurti (132), into three groups: (a) those that show strong Raman lines, for example, the chlorides of Hg, P, As, Sb, C, Si, Ti, Sn, and H; (b) those that show faint Raman lines, BiCl_3 , ZnCl_2 , CdI_2 , AuCl_3 ; (c) and those that show no Raman lines at all, chlorides of Na, K, NH_4 , Ba, Ag, Cu, Cd, Mg, Sn (ous), Th, and Cd, Br_2 , PbI_2 , KI, LiF, NaF, CaF_2 . It is postulated that these distinctions are dependent upon the type of binding, that is, either ionic or covalent. Those halides that are good conductors show no Raman spectra, while those that are nonconductors or feeble

conductors show Raman lines more or less strongly. Mercuric chloride, for example, is very little ionized in solution, and the conductivity of the molten substance is very low. This compound has one strong line, $\Delta\bar{\nu}$ 312, and a faint companion line at $\Delta\bar{\nu}$ 381. It is assumed that the strong line represents a symmetrical vibration of the chlorine atoms towards and away from the central atom in a linear model for the mercury molecule. This bears some similarity to the vibrations of carbon dioxide and carbon disulfide. The weak line is attributed to the oscillations of the chlorine atom against the remainder of the molecule.

The Raman spectrum of mercurous chloride cannot be explained on the basis of a simple HgCl molecule. The stronger line for this substance, $\Delta\bar{\nu}$ 275, is attributed to the symmetrical movement of the chlorine atoms towards and away from the central Hg-Hg group in a linear model

The broad division between ionic and molecular lattices finds a counterpart in the Raman spectra in typical ionic crystals, such as sodium chloride, which shows no vibrational Raman spectrum, while typical molecular substances show prominent lines. Compounds of the type of cadmium iodide probably belong to the transition stage.

While the most abundant naturally occurring crystals are silicates, their very complexity has been something of a deterrent from the point of view of Raman spectra investigations. It has already been pointed out that this method of approach is somewhat empirical in nature, particularly in the case of complicated compounds. It has been necessary, therefore, to lay a substantial foundation before approaching complex silicates.

Nisi (147) points out that according to x-ray analysis in the orthosilicates the SiO_4 group is independent, each oxygen atom combining with one silica atom, as well as being linked to other metal ions, by which the groups are bound together. In other silicates one or more of the four oxygen atoms are shared by two silicon atoms and form silicon-oxygen complexes.

The strongest frequency obtained on examination of the compounds previously mentioned is attributed to the inactive vibration of the SiO_4 group and increases with the valency of the

metal ion as observed in the cases of the sulfates and nitrates. A large frequency shift was noted at about $\Delta\bar{\nu}$ 3650, the origin of which is as yet unknown. A large number of Raman shifts were obtained from most specimens, but the experimental data are too scattered as yet to find any definite relations between crystal structures and the frequency shifts of the Raman lines.

Those minerals containing a PO_4 group have a strong Raman line corresponding to an inactive frequency shift near $\Delta\bar{\nu}$ 1000. The shift is somewhat smaller in the case of the sulfate, notwithstanding the fact that the phosphorus atom is lighter than the sulfur atom. As is to be expected, the PO_4 group shows other similarities with the SO_4 group.

On the whole there is essentially little difference between the Raman spectra from aragonite and from calcite. There may be some differences in intensities. Apparently $\Delta\bar{\nu}$ 188 in calcite is stronger than the equivalent shift in the aragonite. The ratios of intensities of the lines corresponding approximately to $\Delta\bar{\nu}$ 278 and $\Delta\bar{\nu}$ 156 are in a reverse order in the two crystal planes (148). Most of the apparent differences, if any, owe their origins to faint lines which by different observers may be evaluated differently.

As will be seen later, the spectrum of the crystalline hydroxides is consistent with the view that $\Delta\bar{\nu}$ 3630 arises from the oscillation of the hydrogen atom against the oxygen atom. In the solid this vibration is appreciably sharper than in the liquid or in solution. Unfortunately, other than sodium hydroxide, most of the hydroxides investigated have been in the form of the crystal hydrates. This has resulted in a confusion between the O—H vibration of the true hydroxide and that arising from the water of crystallization.

The Raman spectra of inorganic crystals provide, as may be seen, some information concerning the type of interatomic binding, the crystal structure that may be expected, and reference points from which the Raman spectra of solutions and complexes may be more advantageously studied.

V. RAMAN SPECTRA OF WATER

Perhaps the most consistently divergent results with any compound have been obtained in the Raman spectra studies of water. This is attributable to two factors: first, the bands are broad and diffuse and it is difficult to estimate the various maxima; second, the actual magnitudes of the frequency shifts apparently depend on the previous history of the water. This is not unreasonable from a physico-chemical point of view, as water has long been thought to consist of more than one elementary form, usually termed the mono-, di- and tri-hydrol forms, depending on whether the water is polymerized into one, two, or three molecular units. The maximum polymerization has been supposed to occur at the lower temperatures. Regardless of the disagreement among the various observers as to the magnitude of the frequency shifts observed with water, there is a fairly uniform consensus of opinion that the intensity of the maxima is a function of temperature. Furthermore, there is an additional change in aqueous solutions, depending on the solute.

Rao (150) obtained average maxima for water at $\Delta\bar{\nu}$ 3345 and for ice $\Delta\bar{\nu}$ 3223. Later he recorded for water (181) three bands: $\Delta\bar{\nu}$ 3205, 3410, 3582. The first of these decreases in intensity with increasing temperature and the last increases, the middle band remaining constant. The addition of electrolytes causes similar behavior. Ice shows the opposite intensity relations; the $\Delta\bar{\nu}$ 3205 in ice has greater intensity than in water, and the 3582 weaker than in water.

Gerlach (167) and Pringsheim and Schlivitch (178) made similar observations.

Meyer (175) accounted fairly plausibly for the increased broadening and dissymmetry of the water band with increasing temperature on the assumption that water is a mixture of di- and tri-hydrols at lower temperatures, the tri-hydrol being more abundant.

Ganesan and Venkateswaran (166) obtained for water $\Delta\bar{\nu}$ 2355, 3199, 3453, 3609, and 5502, the 2355 band being doubtful. At 80°C. the 3199 band practically disappears, while the 3453

and 3609 bands diminish only slightly in intensity. The decrease in the 3199 band was attributed to depolymerization. For ice these authors found $\Delta\bar{\nu}$ 3193, 3391, 3549, 5393, each band being more narrow than in the case of water. In the case of ice the 3193 and 3391 bands are of approximately the same intensity. With water the 3453 band is more intense than the former. The 5393 band is much brighter in ice than it is in water.

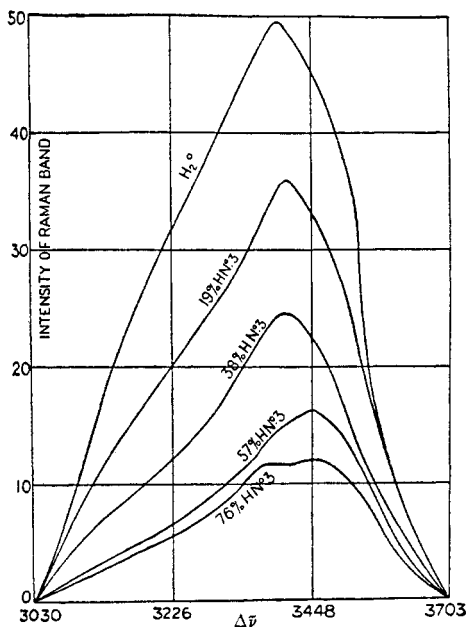


FIG. 8. THE EFFECT ON THE WATER BANDS OF DIFFERENT CONCENTRATIONS OF NITRIC ACID

A splitting of the water band near $\Delta\bar{\nu}$ 3448 into at least two maxima is shown (after Rao).

Rao (182) studied the Raman spectrum of water as a function of temperature, and water solutions of nitric acid as a function of concentration. For pure water he obtained maximum values at $\Delta\bar{\nu}$ 3085, 3420, and 3635. The distribution of intensity in the water bands at 14°C. and 75°C. was determined. With increased temperature there is a diminution of intensity in the 3085 band and an increase in intensity in the 3635 band. This change was

again attributed to a change in the relative proportions of water polymers. According to Rao, a change in the maximum of the 3420 band toward a higher frequency would also indicate a decrease in the number of double molecules.

The changes in intensity distribution with the addition of an electrolyte may also be due to the diminution of the proportion of the triple molecules and to the increase of the single molecules. With high concentrations of nitric acid (76 per cent), however, a second maximum begins to develop which does not appear in the temperature phenomenon (figure 8). This was ascribed to the formation of hydrates; the water molecules, instead of combining among themselves, begin to associate with the molecules of the electrolyte. The heaviness of the ions or molecules with which the water molecule combines results in only a small shift of the water band; hence a second maximum in nitric acid at about 3400 was observed.

Brunetti and Ollano (164) and Ollano (177) stated that the water bands are composed of three elements corresponding to $\Delta\bar{\nu}$ 3225, 3469, 3589, the 3469 being the most intense. These authors stated that the triangular water molecule should have three fundamental frequencies, the absorption spectra indicating two fundamentals, one at $\Delta\bar{\nu}$ 1640 and another at $\Delta\bar{\nu}$ 3360, the third being inactive. If this is true, the inactive frequency should appear in the Raman effect the same as the inactive frequencies of carbonate and nitrate ions. No Raman line at $\Delta\bar{\nu}$ 1640 was observed. The $\Delta\bar{\nu}$ 3225 was attributed to the most polymerized state of water and the $\Delta\bar{\nu}$ 3589 to the least or to water itself. Solutions containing hydrochloric acid or cesium chloride cause a decreased intensity of the 3225 and 3589 bands, while the 3469 band is intensified. This behavior is accounted for on the basis of chloride ions causing a depolymerization of the higher polymers and an increased polymerization of the lighter polymers. In nitrate solutions the 3589 band increases so much in intensity that the middle line $\Delta\bar{\nu}$ 3469 loses its identity. $\Delta\bar{\nu}$ 3225 weakens slowly under these conditions and is absent only in solutions of high concentration. It is concluded that in the presence of the nitrate ion the aqueous solvent depolymerizes but does not become homogeneous.

Segré (183), by excitation with the 2536 A.U. mercury line, which is reabsorbed by mercury vapor, observed a new water band with a maximum displacement of $\Delta\bar{\nu}$ 140, both as Stokes and anti-Stokes lines. Since this can not be attributed to rota-

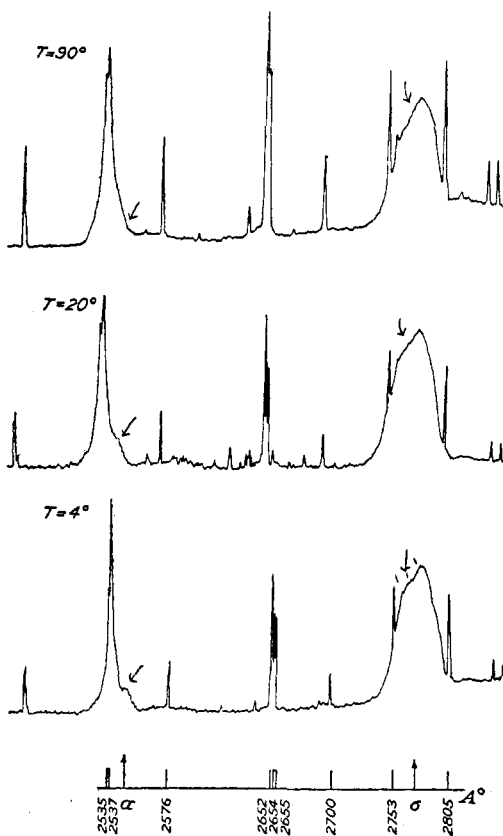


FIG. 9. THE MODIFICATION OF THE WATER BANDS WITH CHANGING TEMPERATURE

Showing a diminution with increased temperature in the intensity of $\Delta\bar{\nu}$ 140, and the three bands near $\Delta\bar{\nu}$ 3220, 3445, and 3630 (after Segré).

tional or vibrational spectra of hydrogen, it was ascribed to the oscillations of the water polymers. On increasing the temperature from 20°C. to 90°C. there is a decrease in intensity of this band (figure 9). Another weak and diffuse band, also sensitive

to temperature at about $\Delta\bar{\nu}$ 600, was observed. The 140 shift is not present in ice. Since the latter is also presumed to be polymerized, this seems somewhat inconsistent.

This low frequency oscillation has also been observed by Bolla (84). The frequency shift has been given, however, as $\Delta\bar{\nu}$ 172 instead of 140. In addition two new lines at $\Delta\bar{\nu} \pm 60$ were observed with the same technique as used by Segré (figure 10). Both Stokes and anti-Stokes lines were observed in all cases. The

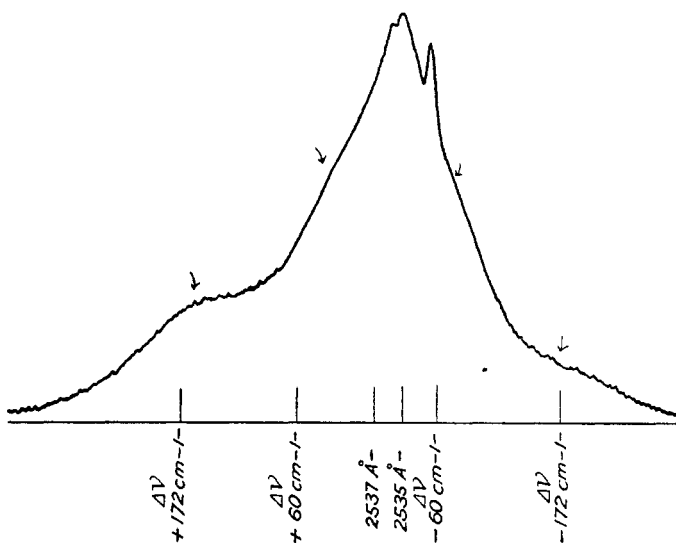


FIG. 10. LOW-FREQUENCY OSCILLATIONS IN WATER ATTRIBUTED TO THE POLYMERS OF WATER
(After Segré)

larger frequency shifts obtained were $\Delta\bar{\nu}$ 3220, 3445, and 3630. These are shown in figure 11.

In addition to these bands Bolla (163) more recently has observed in water at 17°C. $\Delta\bar{\nu}$ 510, 780, 1645, 2150, and 3999, all being very weak, but of this group of lines $\Delta\bar{\nu}$ 1645 is the strongest. Magat (170) reports $\Delta\bar{\nu}$ 190 and 600 as present in water and states that if the three fundamental frequencies of water are $\Delta\bar{\nu}$ 600, 1595, and 3500 it is possible to interpret the absorption spectrum as a combination of fundamental frequencies and their harmonics.

On the basis of quantum mechanics supplemented by spectroscopic data, Van Vleck and Cross (187), Mecke (171) and Mecke, Baumann, and Freudenberg (172, 173, 174) have calculated two of the fundamental frequencies of the water to be near $\Delta\bar{\nu}$ 3600 and 3750, the diffuseness of the bands being attributed to a superposition of the vibrations. The third calculated fundamental lies near $\Delta\bar{\nu}$ 1660. Johnston and Walker (169) measured the Raman spectra of water vapor at 275°C. and observed Raman shifts at $\Delta\bar{\nu}$ 3654, 1648, and 984, the last fundamental being inconsistent with the calculations just mentioned. It is to be remembered that these latter involve considerable approxima-

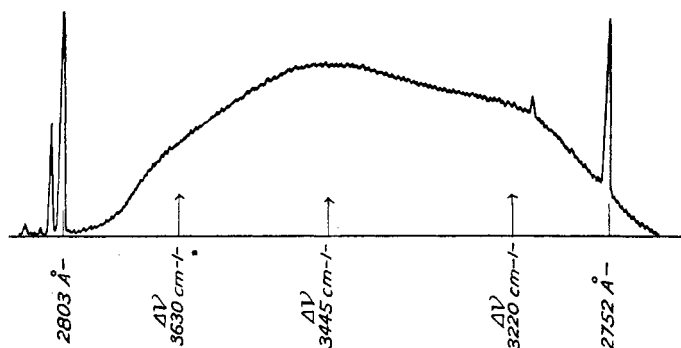


FIG. 11. HIGH-FREQUENCY OSCILLATIONS IN WATER
(After Segré)

tions and are for isolated molecules. The shift at $\Delta\bar{\nu}$ 1654 has been observed by Silveira (184) in the Raman spectrum of salt solutions and was tentatively attributed by him to the water molecule. It is, however, exceedingly weak, and its reality not conclusively established.

Rank (180) observed $\Delta\bar{\nu}$ 3650 in water vapor but could not find $\Delta\bar{\nu}$ 984 and $\Delta\bar{\nu}$ 1648. The shift $\Delta\bar{\nu}$ 984 observed by Johnston and Walker was attributed to a shift of $\Delta\bar{\nu}$ 3650 excited by the 3906 A.U. mercury line. The frequency shift $\Delta\bar{\nu}$ 3654 has also been observed by Daure and Kastler (165) in water vapor.

The largest number of Raman lines for water have been observed by Hulubei (92). He obtained two frequency shifts, $\Delta\bar{\nu}$

3233 weak and 3443 strong. No third component was observed. He attributed a third band found by others to imperfect monochromatism in the exciting sources. In addition to these bands a number of other Raman lines were observed which are represented to be combinations of the fundamental frequencies obtained in infra-red absorption corresponding to 6.26μ and 2.66μ (ν_1 and ν_2). These are as follows:

| | | | | | | | | | | |
|-------------------------|------------------|----------|------|----------|------------------|------------------|----------|-------|-------------------|-------|
| $\Delta\bar{\nu}$ | 6747 | 7246 | 7757 | 8200 | 8660 | 9175 | 9569 | 10039 | 10635 | 10944 |
| μ | 1.48 | 1.38 | 1.29 | 1.21 | 1.154 | 1.09 | 1.05 | 0.99 | 0.94 | 0.91 |
| | $2\nu_1 + \nu_2$ | $2\nu_2$ | | $5\nu_1$ | $3\nu_1 + \nu_2$ | $\nu_1 + 2\nu_2$ | $6\nu_1$ | | $2\nu_1 + 2\nu_2$ | |

These long shifts are nearly completely suppressed in 3 *N* salt solutions. These changes are also analogous to that of the 3233 band and were attributed to variations in the degree of association.

The Raman shift for water at $\Delta\bar{\nu}$ 1705 and 3474 was noted by Kimura and Uchida (128).

Bolla (162), with long exposures and excitation by the 2536 A.U. mercury line, observed nine or ten diffuse components in the water bands.

Rafalowski (179) observed a sharpening of the water band with increasing concentration of nitric acid. With hydrochloric acid the intensity of both outer components decreases with increased concentration while the middle component is broadened.

Hatley and Callihan (168) obtained a water band consisting of three components. The effects on this band of various concentrations of aqueous solutions of potassium chloride, sodium hydroxide, and potassium hydroxide are to cause the tops of the curves to grow sharper with increasing concentration and the energy to shift to the long wave length side (increased λ).

Specchia (185, 186) stated that the water band consists of three components. The effect of temperature is to decrease the intensity of the three components with increasing temperature and to cause a slight displacement towards the lower frequencies of the maxima.

Hibben (125) has pointed out that as the concentration of aluminum chloride or zinc chloride in solution is increased the water band becomes more intense and much sharper, with the maximum at $\Delta\bar{\nu}$ 3418 for the central band. Nisi (176) found two bands for water— $\Delta\bar{\nu}$ 3135 and 3437. Notwithstanding this, the water band—excited by the 4047 A.U. and 3650 A.U. mercury lines—apparently looked like triplets. At temperatures of 100°C. there is not much difference in structure except that the lower frequency shift fades somewhat.

True water of crystallization shows three bands much sharper than those in liquid water. These (138) are $\Delta\bar{\nu}$ 3230, 3400, 3500. Nisi (176) studied the Raman bands due to crystallization in a number of sulfate salts. Most of these show but one band, namely, at approximately $\Delta\bar{\nu}$ 3400. Others such as the pentahydrate of copper sulfate show three bands at $\Delta\bar{\nu}$ 3211, 3377, and 3494, all of which are somewhat sharper than in the case of liquid water. The intensities of the bands in some hydrates such as gypsum vary somewhat, depending upon the direction of observation and illumination of the crystal.

It is difficult to evaluate these results since they are so discordant. It seems probable that some of these differences may be rightfully attributed to differences in degree of polymerization of the water examined. It is also probable that a contributing factor is the misinterpretation of spurious lines as suggested by Hulubei. It is also to be admitted that no accurate evaluation of the maxima can be reached except by microphotometric means, which have not always been employed. Notwithstanding these allowances, there still remain some unexplained discrepancies. Some observers find only two bands. The preponderance of evidence, however, is in favor of at least three of the higher frequency components. The behavior with temperature is also a matter of question, with the evidence approximately equally divided between an increase and a decrease in the $\Delta\bar{\nu}$ 3590 band. Presumably, however, the 3220 band decreases in intensity with increased temperature. It is a fact that the addition of electrolytes to aqueous solutions profoundly modifies the general character of the water band, particularly with increased concentration.

It is, furthermore, possible that this modification may be somewhat different with different types of electrolytes. This modification of symmetry is also equally apparent in the water of crystallization. How this may change with temperature is as yet undetermined, as is the number of water bands to be expected. The existence of low frequency oscillations, as noted by Segré and also by Bolla, $\Delta\bar{\nu}$ 60, 140 (172), is of considerable interest if they can be definitely shown to be due to the oscillation of water polymers. The large frequency shifts observed by Hulubei are consistent with the infra-red absorption spectra but have not been noted by other observers.

The essential fact brought out in these investigations is the anomalous behavior of water under different conditions of temperature and of electric environment (containing a solute). This has been most logically explained on the basis of changes in the molecular aggregations of which water consists, and is compatible with similar conclusions derived from other physico-chemical evidence.

VI. THE RAMAN EFFECT IN ACIDS AND BASES

One of the most fruitful applications of the Raman effect is in the investigation of the constitution of acid solutions of varying concentrations. While conductivity measurements and determinations of hydrogen-ion concentrations by various methods have given a picture of the stepwise dissociation of polybasic acids as well as the fraction of undissociated molecules remaining in solution, practically no such method has any meaning in solutions of high concentration. The Raman method, on the contrary, can be applied to solutions from 100 per cent acid to those of a few per cent. Not only is it possible to follow a normal dissociation phenomenon, but it is also possible to distinguish and identify the appearance of other molecular species which may be coëxistent. These data are obtained from the following consideration. In the experiment, if the exposure time is increased in proportion to dilution, the intensity of the Raman lines characteristic of the substance examined will remain constant, provided there is no intervention of another factor. If, however,

dilution or concentration under these conditions causes a change in the molecular configuration or constitution of the acid, there will result a corresponding anomalous Raman effect.

Nitric acid

Such a system has been investigated by Rao (213, 214). Nitric acid was studied in concentrations ranging from 65 per cent acid to 9.7 per cent. The most concentrated acid yielded $\Delta\bar{\nu}$ 1299, 1110, 1046, 957, 685, 638. Of these $\Delta\bar{\nu}$ 638, 685, and 1046 were attributed to the nitrate ion. The remainder, $\Delta\bar{\nu}$ 957, 1110, and 1299, were attributed to the undissociated nitric acid molecule. In addition, $\Delta\bar{\nu}$ 3202, 3427, and 3439–3525, belonging to water were observed. A fourth long-frequency shift, $\Delta\bar{\nu}$ 3321, was also attributed to the undissociated acid. The results are given in figure 12. In this figure the horizontal line at the top of each curve represents complete blackening of the photographic plate. The maxima, marked with a downward arrow, correspond to the undissociated HNO_3 molecules, their intensity diminishing so rapidly that they are almost extinct in the fourth curve, corresponding to a concentration of 39 per cent. The maxima, denoted by an upward arrow, are for the nitrate ion lines, which very rapidly increase in intensity up to 39 per cent concentration. These then diminish again, showing that on initial dilution the dissociation increases much more rapidly than the diminution in concentration, but after a certain stage the dissociation increase becomes less in proportion to diminution in concentration of the ions. It can also be seen that the intensity of the continuous spectrum increases with dilution.

From the relative intensities of the lines ascribed to nitrate ions it is possible to calculate the degree of dissociation and compare it with that obtained by other methods, namely, conductivity and viscosity. This is given in figure 13, in which the lowest curve has been obtained from viscosity-conductivity data, the middle from Kohlrausch's conductivity formula, and the upper from measurements of Raman lines for the nitrate ion. The departures from the Raman method curve are ascribed by Rao to

the inapplicability of standard methods to measure the true degree of dissociation even at moderate concentrations.

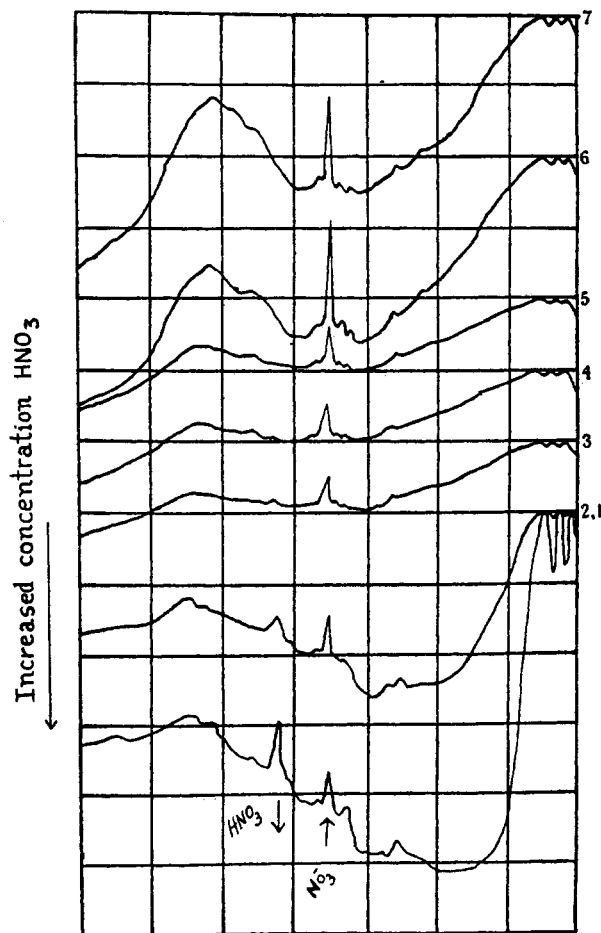


FIG. 12. CHANGES IN THE CHARACTERISTIC RAMAN FREQUENCIES OF NITRIC ACID WITH VARYING CONCENTRATION

Showing increase in nitrate ions and decrease in nitric acid molecules with dilution (after Rao).

The picture, however, is not quite so simple as has just been painted. Kinsey (204) finds in nitric acid solutions, with the

exception of $\Delta\bar{\nu}$ 3321 and $\Delta\bar{\nu}$ 1110, approximately the same lines as observed by Rao. These wave number shifts are $\Delta\bar{\nu}$ 618, 669, 937, 1034, and 1293. Of these, $\Delta\bar{\nu}$ 618 and 669 (Rao's $\Delta\bar{\nu}$ 630 and 689) behaved in exactly the same manner as $\Delta\bar{\nu}$ 937 and 1293, disappearing completely in a 25 per cent solution. This, then, is tacitly attributing the first two of these lines not to the nitrate ion but to the HNO_3 molecule. The 3321 shift noticed by Rao is attributed to excitation by 3650 A.U. mercury line and would

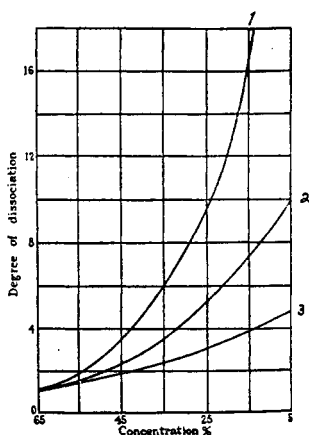


FIG. 13. DEGREE OF DISSOCIATION OF NITRIC ACID AS DETERMINED BY THE RAMAN EFFECT

Curve 1 represents the degree of dissociation as determined from the intensity of the nitrate ion lines, curve 2 the dissociation from conductivity measurements, and curve 3 the dissociation from viscosity-conductivity measurements (after Rao).

correspond to a shift between $\Delta\bar{\nu}$ 618 and 669 if this were the source of the excitation.

Woodward (223, 225) investigated quantitatively the behavior of concentrated nitric acid solutions on dilution. An anomaly revealed by the Raman spectrum was also observed by him. His interpretation, however, differs slightly from that of his predecessors. Solutions containing 14 moles, 9.6 moles, 5.2 moles, and 1.5 moles of nitric acid per liter were examined. The 14 molar solution yields $\Delta\bar{\nu}$ 1311 strong, 1048 very strong, 961 medium, 697 weak, and 643 weak. The line corresponding to $\Delta\bar{\nu}$

1048 was attributed to the nitrate ion. $\Delta\bar{\nu}$ 1311, 961, 697, and 643 are attributed by Woodward to undissociated nitric acid. These increase in intensity with increase of the concentration. At the same time there is a decrease in the $\Delta\bar{\nu}$ 1048 associated with the nitrate ion. In principle this is much the same result as obtained by Rao and Kinsey. Woodward likewise does not find $\Delta\bar{\nu}$ 3321. The change in ionization was further found not to be a function of temperature, since the lines did not change in intensity with experiments carried out at 5°C. and 75°C. The Raman spectrum of nitric acid molecules is more nearly similar to that of nitrate crystals than to the free ion.

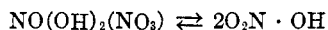
Dadieu and Kohlrausch (194) have investigated the Raman spectra of highly concentrated nitric acid solutions with particular reference to the constitutional form of nitric acid. From an examination of organic and inorganic nitrites and nitrates they conclude that the internal oscillations of the nitro group have the following frequencies,

| | | |
|-------------------------|-----------------------------|----------------------------|
| Ar · NO ₂ | $\Delta\bar{\nu}_1 = 1520,$ | $\Delta\bar{\nu}_2 = 1340$ |
| R · NO ₂ | $\Delta\bar{\nu}_1 = 1560,$ | $\Delta\bar{\nu}_2 = 1380$ |
| R · O · NO ₂ | $\Delta\bar{\nu}_1 = 1627,$ | $\Delta\bar{\nu}_2 = 1274$ |

in which $\Delta\bar{\nu}_2$ is the more intense. This leads to the conclusion that $\Delta\bar{\nu}$ 1300, found in the nitric acid solutions, can be explained by the fact that a not inconsiderable portion of the dissolved nitric acid assumes the formula HO · NO₂. However, if this is the case, it must be first demonstrated that a second frequency at about $\Delta\bar{\nu}$ 1625, also known to belong to the NO₂ group, is present, and last, that the spectrum of nitric acid with increasing concentration must approach near to the type of spectrum found in the organic nitrate R · O · NO₂. The results are given in table 6.

The $\Delta\bar{\nu}$ 1038 is attributed to the nitrate ion. The appearance of $\Delta\bar{\nu}$ 1665 and 1687 is confirmatory of the existence of the ester or pseudo-acid form of nitric acid. Frequencies corresponding to C—H oscillations are omitted in the table. The line corresponding to $\Delta\bar{\nu}$ 3420 would be attributed to the homopolar O—H binding, but is considered uncertain.

A similar line of reasoning has been given by Brunetti and Ollano (191, 192). They assume that one may have an equilibrium in the acid solution as given by Hantzsch (200).



On this theory, by adding water one obtains the hydrate of the pseudo-acid $\text{O}_2\text{N} \cdot \text{OH} \dots \text{H}_2\text{O}$, salts of the hydroxonium type, $(\text{NO}_3)\text{H}_3\text{O}$, salts of the polyhydroxonium type, $(\text{NO}_3)(\text{H}(\text{H}_2\text{O})_n)$, and hydrates of the ions of this salt, $(\text{NO}_3)(\text{H}_2\text{O})^-$ and $(\text{H}(\text{H}_2\text{O})_n)^+$.

TABLE 6
Concentrated nitric acid and organic nitrates

| I HNO_3 (64 per cent) | II HNO_3 (100 per cent) | III $\text{H}_3\text{C} \cdot \text{O} \cdot \text{NO}_2$ |
|--------------------------------------|--|--|
| — | — | 353 |
| 635 | 607 | 580 |
| 684 | 667 | 663 |
| 949 | 916 | 860 |
| — | — | 994 |
| 1038 | — | — |
| — | — | 1170 |
| 1302 | 1292 | 1276 |
| 1625 | 1665} | 1630 |
| 1668 | 1687} | |
| — | [3420] | |

Hence radiation should be found due to the NO_2 and NO_3 groups and to NO_3 ions and H_3O ions. To the NO_2 group were ascribed the frequencies $\Delta\bar{\nu}$ 815, 1241, and 1236. To the NO_3 ions were ascribed $\Delta\bar{\nu}$ 717, 1049, and 1389. Concentrated nitric acid solutions were next examined in concentrations varying from 13.4 moles to 2.7 moles in eight steps.

The results of Brunetti and Ollano may be summarized as follows: all nitric acid solutions exhibit $\Delta\bar{\nu}$ 1045 and 1395, weak in the dilute solutions. At less than 10 molar there is also present $\Delta\bar{\nu}$ 716, all these frequency shifts being in common with the nitrates. The frequencies characteristic of the NO_3 group diminish in intensity as the solution becomes less concentrated in nitrate ions.

In the more concentrated solutions other frequencies are noted, particularly one at $\Delta\bar{\nu}$ 1306, similar in aspect to $\Delta\bar{\nu}$ 1326 in the nitrites but certainly displaced about twenty wave numbers. However, when this line is most intense, $\Delta\bar{\nu}$ 815 and 1240, characteristic of the nitrites, are not present. Furthermore, $\Delta\bar{\nu}$ 1306 (NO_2) disappears at concentrations of 7 molar or approximately 25 per cent.

In addition to the frequencies cited, $\Delta\bar{\nu}$ 640, 690, and 950 are also obtained, intense in concentrated solutions and disappearing on dilution. In 65 per cent nitric acid and somewhat less, $\Delta\bar{\nu}$ 1138 was also observed. Brunetti and Ollano concluded that the presence of the frequency $\Delta\bar{\nu}$ 1306, together with a strong water band at $\Delta\bar{\nu}$ 3589, justifies the opinion that there exists in aqueous nitric acid not only $\text{O}_2\text{N}\cdot\text{OH}$ but also an aggregate of the form $\text{O}_2\text{N}\cdot\text{OH}\cdot\text{H}_2\text{O}$. The value of the concentration at which the NO_2 frequency disappears (under 7 molar) is in accord with the calculations of Hantzsch (201). In concentrated solutions, therefore, the nitrate ions do not manifest themselves as such but rather as NO_2 groups.

The foregoing discussion represents the more recent developments in the determination of the constitution of nitric acid. It is certain that the factual data demonstrate the existence of an anomalous behavior. It is equally certain that the Raman effect method is one of the most logical means of investigating this behavior. It is probable that most of the conclusions drawn are in accordance with facts. The Raman effect evidence probably gives a fairly close picture of the actual ionization process. It is also probable that the formula HNO_3 does not represent the true constitution of nitric acid. It is more than possible that in higher concentrations the acid is more accurately represented by the formula $\text{HO}\cdot\text{NO}_2$. What divergent results there are in these experiments are mainly due to ambiguous interpretations and to the failure to use a proper monochromatic source of radiation. The overlapping of the water bands has added not a little to the confusion. While the constitution proposed by Hantzsch and adopted by Brunetti and Ollano may have considerable foundation, the actual experimental results provide little or no data

upon which the existence of H_3O^+ and salts of the polyhydroxonium type may be predicated.

Sulfuric acid

The first Raman investigations of sulfuric acid were more concerned with the number of Raman lines obtainable than with any anomalous effects to be observed with dilution (155, 167, 219, 221).

Some of these early investigators reported wave-number shifts between approximately $\Delta\bar{\nu}$ 2000 and $\Delta\bar{\nu}$ 2300. These are probably erroneous. Later, more accurate determinations at different concentrations were made. Nisi (208) obtained at least seven characteristic fairly strong Raman bands, for example, in 10 per cent solutions, $\Delta\bar{\nu}$ 432, 598, 893, 978, 1046, and 1200. A 75 per cent solution gave $\Delta\bar{\nu}$ 417, 578, 913, 1035, 1167, and 1313. Pure H_2SO_4 gave $\Delta\bar{\nu}$ 414, 564, 740, 911, 1043, 1170, 1366, 1517. Of these $\Delta\bar{\nu}$ 911 is the strongest in the concentrated state, but the intensity of this band and the continuous background spectrum gradually fall off with dilution. This is attributable to H_2SO_4 molecules. The band of about $\Delta\bar{\nu}$ 1040 becomes strong rapidly with addition of a small quantity of water. The band of $\Delta\bar{\nu}$ 980 begins to appear only when the acid is diluted to approximately 50 per cent, and increases with dilution. These two bands, viz., 980 and 1040, are attributed to the SO_4^- and HSO_4^- groups, respectively. The diffuse bands $\Delta\bar{\nu}$ 1170, 564, and 414 increase slightly in wave-number shift with decrease in concentration. These three bands appear frequently in sulfate solutions. The band at $\Delta\bar{\nu}$ 1366 appears only in concentrated solutions.

Woodward (223, 225) has also quantitatively examined the Raman spectrum of sulfuric acid as a function of concentration. These experiments were carried out in a more quantitative fashion, since exposure was made proportional to the dilution. A similar anomalous behavior was observed. For a 10 per cent solution he obtained $\Delta\bar{\nu}$ 437, 613, 985, 1048, and 1205; for 75 per cent, $\Delta\bar{\nu}$ 432, 588, 912, 1043, and 1163; for 100 per cent, $\Delta\bar{\nu}$ 400, 560, 908, 1143, and 1359. With decreasing acid concentration there is an increase in the intensity of $\Delta\bar{\nu}$ 1048. At the same

time there is a marked decrease in $\Delta\bar{\nu}$ 908, the strongest line of the pure acid. In acids of medium concentration, that is, approximately 25 to 50 per cent, there appears a line $\Delta\bar{\nu}$ 982 not present in the more concentrated solutions. This increases in intensity with dilution. These changes are depicted in figure

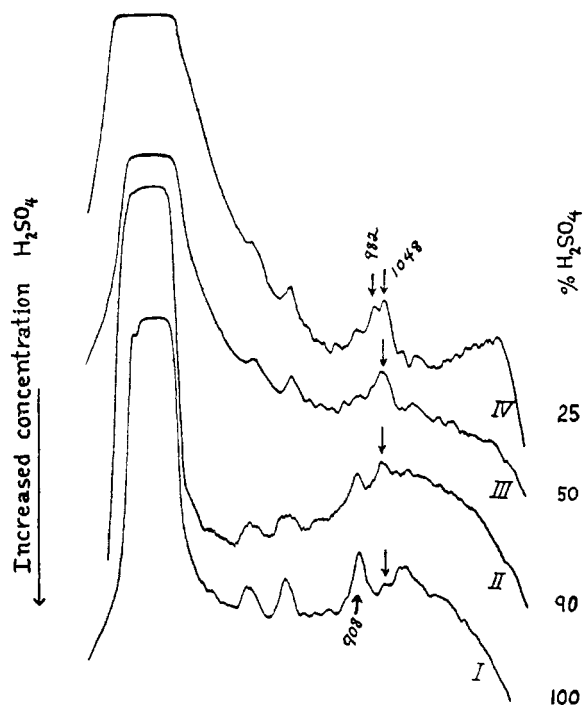


FIG. 14. CHANGES IN THE CHARACTERISTIC RAMAN FREQUENCIES OF SULFURIC ACID WITH VARYING CONCENTRATIONS

$\Delta\bar{\nu}$ 908 characteristic of sulfuric acid molecule decreasing in intensity with dilution; $\Delta\bar{\nu}$ 1048 characteristic of HSO_4 ion, and $\Delta\bar{\nu}$ 982 characteristic of SO_4 ion increasing in intensity with dilution (after Woodward).

14, where curve I corresponds to 100 per cent, curve II to 90 per cent, curve III to 50 per cent, and curve IV to 25 per cent sulfuric acid. These alterations in intensity are reasonably explicable if one assumes that $\Delta\bar{\nu}$ 908 is associated with the H_2SO_4 molecule and hence decreases in intensity with increased dilution. This presupposes that the concentration of H_2SO_4 , as such, decreases

owing to ionization. On the other hand, $\Delta\bar{\nu}$ 1048, on the average, is associated with the HSO_4 ion. The production of HSO_4 ions as a first step in the ionization process would give an increase in intensity of this line with dilution. Furthermore, $\Delta\bar{\nu}$ 982 is presumed to be associated with the SO_4 ion. This appears only in fairly dilute solutions as a result of the dissociation of HSO_4 into SO_4 ions and hydrogen ions. This naturally likewise increases in intensity with dilution. This is somewhat confirmed by a study of the Raman spectrum of KHSO_4 which gives $\Delta\bar{\nu}$ 1056, 982, and 593, the former two being moderately strong. $\Delta\bar{\nu}$ 982 is present in all sulfates.

The line corresponding to the shift $\Delta\bar{\nu}$ 1048, presumably characteristic of the HSO_4 ion, is found to be moderately strong in the Raman spectra of pure acid as determined by Nisi, while completely absent in the observations of Woodward. The latter remarks, however, that the addition of only a small quantity of water to the pure acid evokes this line, and it is presumed that the acid used by Nisi contained small quantities of water.

Bell and Fredrickson (190) made somewhat similar observations. The $\Delta\bar{\nu}$ 1048 increases in intensity with dilution. The $\Delta\bar{\nu}$ below this value apparently decreases in intensity with dilution. At approximately 40 per cent, $\Delta\bar{\nu}$ 1200 appears and persists in dilute solutions. A change in the intensity of $\Delta\bar{\nu}$ 1048 is attributed, perhaps, to a hydrated hydrogen ion. The intensity variations, however, were estimated only by visual inspection.

Fadda (198) found that concentrated sulfuric acid shows none of the characteristic frequencies of the SO_4 group, but in all concentrations less than 25 per cent the spectrum shows $\Delta\bar{\nu}$ 984, which is the most intense in the sulfates.

The effect of an electric field on a 50 per cent solution of sulfuric acid was determined by Ricca (215). When the direction of the current is such that the hydrogen ions move toward the spectrograph, the higher frequency end of the bands is broadened. With the current in a reverse direction the shift is in the opposite direction.

Specchia (218) noted that in solutions of sulfuric acid there is a progressive displacement with dilution of the Raman lines to-

ward greater wave lengths. A decrease in the intensity of $\Delta\bar{\nu}$ 892 and an increase in intensity of $\Delta\bar{\nu}$ 1052 were observed with dilution. At low concentrations of acid (13.5 per cent) no substantial modification in the essential characteristics of the Raman spectra of the acid was observed.

The results with sulfuric acid obtained by different observers are more concordant than those in the case of nitric acid. In the main, they point fairly clearly to the stepwise dissociation of sulfuric acid with dilution by means of the initial formation of HSO_4 ions and the latter's subsequent dissociation into SO_4 ions. The actual molecular constitution of the acid is still a nearly unknown entity. One thing is definite, however, namely, that the hydrogens in sulfuric acid are hydroxyl hydrogens, since the characteristic S—H shift is approximately 2600 wave numbers, a shift which is not present in any of these salt or acid solutions.

Sulfurous acid

The spectrum of sulfurous acid as measured is not completely different from that of sulfuric acid. An analysis of the results obtained by Fadda (198) gives a very interesting insight into the constitution of this acid. The $\Delta\bar{\nu}$ obtained were 569, 1047, 1142, and 1199, of which $\Delta\bar{\nu}$ 1142 was the most intense. These results were compared by Fadda with the $\Delta\bar{\nu}$ obtained from sulfates, acid sulfates, and sulfites. These are given in table 7.

It is immediately apparent that there is no common likeness between the spectrum from sulfurous acid and that from sodium sulfite or sodium sulfate. Two shifts, namely, $\Delta\bar{\nu}$ 569 and $\Delta\bar{\nu}$ 1047, are similar to those obtained in the acid sulfates. The presence of these lines was therefore attributed to the oxidation of a part of the sulfurous acid to sulfuric. The $\Delta\bar{\nu}$ 574 in sulfuric acid is not a constant value but changes slightly in frequency from $\Delta\bar{\nu}$ 561 for a 100 per cent solution to $\Delta\bar{\nu}$ 613 in a 10 per cent solution. $\Delta\bar{\nu}$ 569, therefore, falls within the range of $\Delta\bar{\nu}$ given by HSO_4 ions as determined from the Raman spectra of sulfuric acid. Most significant is the shift $\Delta\bar{\nu}$ 1142. This frequency is the characteristic one for sulfur dioxide (111, 202, 197, 209). $\Delta\bar{\nu}$ 1199 can perhaps be attributed to a shift characteristic of an

HSO_3 ion, but this is incapable as yet of direct substantiation. The absence of a line corresponding to approximately $\Delta\bar{\nu}$ 450 is without other explanation than an intensity factor.

For sulfurous acid Nisi (209) observed $\Delta\bar{\nu}$ 427, 528, 1017, 1054, 1152 and 1337, of which $\Delta\bar{\nu}$ 1337 was considered very strong. $\Delta\bar{\nu}$ 1054 was attributed to the HSO_3 ion.

The summary conclusion from these data, therefore, is that, on the whole, sulfurous acid does not exist as such in solution, but, on the contrary, retains the characteristics of sulfur dioxide except for a fraction which may be oxidized by atmospheric oxygen

TABLE 7
Sulfates, sulfites, acid sulfates, and sulfurous and sulfuric acids

| Na_2SO_3 | Na_2SO_4 | KHSO_4 | H_2SO_3 | H_2SO_4^* |
|--------------------------|--------------------------|-----------------|-------------------------|---------------------------|
| 471 | 460 | 427 | 569 | 421 |
| 602 | 617 | 593 | 1047 | 574 |
| 984 | 984 | 978 | 1142 | 985 |
| — | 1104 | 1047 | 1199 | 1047 |

* Incomplete.

to form sulfuric acid. This is consistent with conclusions already drawn from infra-red absorption investigations (217).

Hydrochloric and other halogen acids

The Raman spectrum of hydrochloric acid has been investigated as a function of concentration (167). There are no lines attributable to HCl, but a marked decrease was noted in the width of the water band with the increasing concentration of hydrochloric acid. Other observers (116, 196) have found no Raman lines in hydrochloric acid solutions, although $\Delta\bar{\nu}$ 2885 has been observed for gaseous hydrogen chloride (222) and $\Delta\bar{\nu}$ 2781 for liquid HCl (216). These results are to be expected if the HCl is completely ionized in solution. In both the liquid and gaseous states the binding is homopolar and would consequently give rise to a value corresponding to the linear vibrations of hydrogen-chlorine.

Woodward (223, 225) reinvestigated the Raman spectrum of

hydrochloric acid in concentrated aqueous solution and in organic solvents, such as benzene, xylene, and carbon tetrachloride, but could find no evidence of any associated hydrochloric acids.

He also investigated the Raman spectrum of hydrofluoric acid (40 per cent). It is well-known that this acid is polymerized in the vapor phase, and conductivity measurements would indicate the presence of an HF_2 ion from the dissociation of H_2F_2 (195, 188). No Raman lines were observed. However, a strong continuous background spectrum is present which tends to mask any weak Raman lines. In spite of this fact, it is surprising that no lines were elicited if hydrofluoric acid has the constitution generally attributed to it. It is probable that this material will be reinvestigated and this point clarified.

Other inorganic acids, such as iodic acid (134, 208, 196, 225, 223) and perchloric acid (208, 210, 219) have been investigated. Krishnamurti found for iodic acid $\Delta\bar{\nu}$ 327, 633, 713, 781, the last three $\Delta\bar{\nu}$ being designated as strong. Nisi observed in a weak solution $\Delta\bar{\nu}$ 317, 393, 799, 805, the first two $\Delta\bar{\nu}$ being weak, $\Delta\bar{\nu}$ 799 medium, and $\Delta\bar{\nu}$ 805 strong. Woodward (225) obtained $\Delta\bar{\nu}$ 335, 649, 796, the last two being strong, the other one medium. Dickinson and Dillon (196) obtained $\Delta\bar{\nu}$ 800 strong and $\Delta\bar{\nu}$ 329 medium in a 45 per cent solution. There are some discrepancies in these results, but none of the experiments were carried out under comparable conditions. The absence of a line at $\Delta\bar{\nu}$ 649 in the dilute solutions may or may not have some significance. It is presumed by Woodward that in 10 *N* solutions the iodic acid is completely dissociated. A thirty per cent solution of perchloric acid gave the following lines according to Nisi: $\Delta\bar{\nu}$ 464, 628, 932, 1115, $\Delta\bar{\nu}$ 932 being strong and the remainder of medium intensity. These results are confirmed by Ollano (177), who obtained $\Delta\bar{\nu}$ 461, 627, 936, and 1118 for the ClO_4 ion in perchloric acid (6 moles per liter), by Dickinson and Dillon (196), who obtained $\Delta\bar{\nu}$ 470, 634, and 935 (strong) in a 60 per cent solution, and by Taylor (219). A strong, wide band appearing at $\Delta\bar{\nu}$ 3550 and a weaker band at 3590 were ascribed by Ollano to hydroxonium (H_3O)⁺ and polyhydroxonium ($\text{H}(\text{H}_2\text{O})_n$)⁺ ions, respectively. As has been mentioned in the discussion of the Raman spectra of water,

the latter conclusion is to be accepted with caution. This becomes still more evident after consideration of the Raman spectra of hydroxides. That acids, salts, and alkalis have an influence on the water band is undoubted, but the attributing of an ill-defined band to a particular homopolar linkage without statistical data as to the origin of that particular frequency, and without other supplementary evidence, is actually extrapolating beyond the experimental information given.

Selenic acid is presumed by Pringsheim and Yost (212) to have some similarity in structure to sulfur trioxide. It gives $\Delta\bar{\nu}$ 695-885.

Phosphoric and phosphorous acids

Solutions containing 25, 50, and 84 per cent phosphoric acid were examined by Nisi (208). He obtained $\Delta\bar{\nu}$ 356, 498, and 911 in the highest concentration, $\Delta\bar{\nu}$ 512, 906 in the medium concentration, and $\Delta\bar{\nu}$ 505, 898 in the more dilute solution. The largest wave-number shift was the strongest, the others medium and diffuse. It is quite uncertain whether the change in $\Delta\bar{\nu}$ with concentration has any real significance. It was suggested that the lines owe their origin to the H_2PO_4 group.

The Raman spectrum of phosphorous acid has been determined by Ghosh and Das (199). The $\Delta\bar{\nu}$ obtained were 672, 940, and 1012, the 940 being the strongest. The lines were attributed to an H_2PO_3 ion. Neither of these acids has been very carefully investigated. The lines are somewhat broad, and in concentrated solutions there is a strong continuous spectrum (124).

Hydrolysis of acid salts

Krishnamurti (205) has investigated the hydrolysis of salts into the free base and free acid. There are three possibilities: namely, hydrolysis of (a) weak bases and strong acids, (b) weak acids and strong bases, (c) weak acids and weak bases. It is necessary to choose a case where the degree of hydrolysis is fairly large and where the molecule of the base or acid has at least one strong line different from that of the salt. It was found that the case of a weak base and strong acid is most favorable. Urea hy-

drochloride in concentrated aqueous solution gives one strong line at $\Delta\bar{\nu}$ 1016 and two weak lines at $\Delta\bar{\nu}$ 513 and 578. Urea itself gives one strong line at $\Delta\bar{\nu}$ 999 and two weak lines at $\Delta\bar{\nu}$ 533 and 1158. In a 4 *N* solution of the salt the same lines persist as for concentrated urea hydrochloride, but on further dilution $\Delta\bar{\nu}$ 999 appears and increases in intensity until it is approximately equal to that of $\Delta\bar{\nu}$ 1016. This appearance of the strong line characteristic of urea is attributed to the progressive hydrolysis of the salt.

Raman spectra of hydroxides

Krishnamurti (96) observed the Raman spectra of sodium, strontium, and barium hydroxides. Of these only sodium hydroxide gave a line which could be ascribed with any degree of certainty to the hydroxide group. This shift is $\Delta\bar{\nu}$ 3630. Woodward (224) obtained in 10 to 12 *N* sodium and potassium hydroxide solutions $\Delta\bar{\nu}$ 3615, together with a strong continuous spectrum also observed by Bär (189). This line is broad and diffuse and comparable with the value $\Delta\bar{\nu}$ 3603 observed by Nielsen (207) and also by Thompson and Nielsen (220).

The magnitude of this shift is of the same order as that attributed to the H \longleftrightarrow O vibration by $\Delta\bar{\nu}$ 3388 in methyl alcohol (193) and $\Delta\bar{\nu}$ 3420 for the H \longleftrightarrow O vibration in ethyl alcohol (203). Nielsen has pointed out that if one assumes the vibration frequencies can be expressed by the formula given by Mecke (206), two vibration frequencies are obtained which do not deviate much from each other. He concludes that it is not improbable that $\Delta\bar{\nu}$ 3603 belongs to OH ions and that the great width of the ordinary water band is related to the hydration of these ions in water. The effect of increased concentration of sodium hydroxide is shown in figure 15.

Hatley and Callihan (168) obtained three bands for water, namely, $\Delta\bar{\nu}$ 3228, 3435, 3624, and studied the displacement of these bands as a function of sodium and potassium hydroxide concentrations, varying between approximately 1 *N* and slightly greater than 10 *N*. It was observed in both cases that with increased concentration the center of gravity of the water band

shifted towards higher frequency, that is, $\Delta\bar{\nu}$ 3624, which became much stronger with increasing concentration of alkali, the inference being that the water and hydroxyl bands are practically identical, particularly with reference to the highest band observed for water.

It has been tentatively suggested by Carrelli, Pringsheim, and Rosen (116) that one of the lines observed in ammonium hydroxide solution ($\Delta\bar{\nu}$ 3385) might be attributed to the OH ion. Woodward contends that it is more likely that this frequency would be

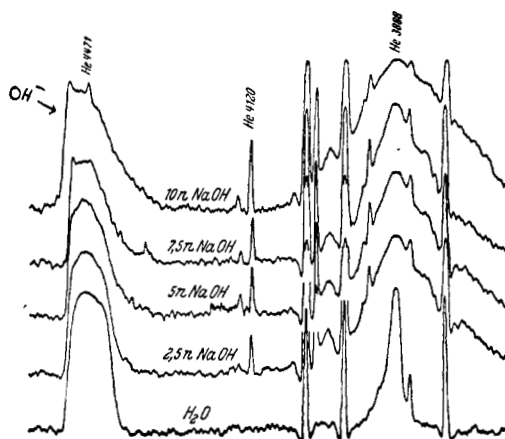
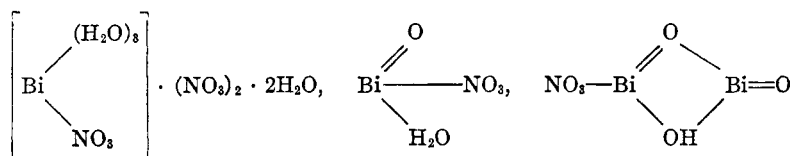


FIG. 15. RAMAN BANDS FOR WATER AND OH IONS WITH VARYING CONCENTRATIONS OF SODIUM HYDROXIDE

Showing persistence of OH band in concentrated solutions of sodium hydroxide (after Nielsen).

attributed to an undissociated OH group rather than the ion. This explanation, however, does not seem very plausible, since if this were the origin there should also be a reasonably strong frequency corresponding to the $N \longleftrightarrow OH$ vibration in undissociated ammonium hydroxide as well as $H \longleftrightarrow O$ in the same group. This latter argument is somewhat substantiated by the fact that hydroxylamine hydrochloride shows such a frequency (89) at $\Delta\bar{\nu}$ 995.

It is presumed by Ollano (24) that bismuth nitrate hydrolyzes in the presence of nitric acid to compounds to which he assigns the following structures:



The nitrate ion is in part ionized and in part attached directly to bismuth. It is postulated that aqueous nitric acid solutions of bismuth nitrate contain NO_3^- , Bi^{+++} , BiOH^{++} , and Bi(OH)_2^+ . With diminishing concentration of the acid the concentration of the bismuth ions and BiOH^{++} decreases, while that of Bi(OH)_2^+ increases. The spectrograms give in addition to the lines attributable to the nitrate ions $\Delta\bar{\nu}$ 3595, 1600, and 1500. Of these shifts, $\Delta\bar{\nu}$ 1600 at the lower concentrations has medium intensity, and $\Delta\bar{\nu}$ 1500 always appears intense and sharp. The last two frequencies are assigned to Bi(OH)_2^+ and BiOH^{++} groups, respectively. The frequency $\Delta\bar{\nu}$ 3595 is assigned to the $\text{H} \longleftrightarrow \text{O}$ vibration. $\Delta\bar{\nu}$ 1236 is without assignment.

These allocations of wave-number shifts to specific molecular structure are admittedly somewhat arbitrary in view of the scant experimental data upon which they are predicated.

VII. THE RAMAN SPECTRA OF SOLUTIONS

The Raman spectra method of investigation, when applied to solutions, provides considerable information in regard to the molecular constitution of such systems. It is in no wise unreasonable to expect the same general type of spectrum to be elicited from a solute as would be obtained from its crystalline state of aggregation. The carbonate ion, for example, exists as such in the crystalline state and in solution, and consequently has a similar spectrum. In general, there are, however, certain pertinent differences: namely, the lines corresponding to lattice vibrations are totally absent in the solute, as is to be expected if the dissolved compound is ionized to any reasonable extent; the influence of the cation should be considerably less in solution for similar reasons; and complex ion or complex-compound formation in solution will result in definite anomalies. Polyatomic

ionic groups may be treated, as a first approximation, in the same manner as a gas consisting of the same number of atoms arranged in the same type of spacial configuration. The effect of the solute on the Raman spectrum of the solvent is by no means insignificant, as has been discussed in the Raman spectra of water. The rôle played by the solvents and its influence on the Raman spectrum of the solute due to changing electrical environment are likewise frequently not entirely negligible.

As a preliminary to the discussion, the Raman spectra obtained from most of the inorganic solutions so far studied are given in tables 8 to 16. The spectra obtained from carbon and nitrogen compounds and inorganic complexes will receive special treatment. In these tables some of the relative intensities are indicated by the subscripts s, m, and w, denoting strong, medium, and weak. In most cases these are visual estimates. Where no indications are given, either no estimates were available or the intensities were faint. When only one shift is recorded this is probably the most intense one. It is obvious that there is some divergence in opinion in regard to the weaker lines, particularly when those lines are rather broad. The absence of the proper number of Raman lines for a given configuration is probably indicative of a failure to elicit these lines rather than their actual absence. The wave-number shifts enclosed in parentheses are somewhat doubtful and those followed by a question mark are very doubtful.

A. TYPE AO_2

In examples where the number of Raman lines equal or exceed the minimum requirement, there may be some real differences of opinion, for example in the case of sodium nitrite, where Brunetti and Ollano (191) differ from Carrelli, Pringsheim, and Rosen (116), both as to the magnitude of the shifts and their number.

In general, molecules of the type containing a non-linear triatomic ion should give three fundamental oscillations. This number may be exceeded owing to degeneracy, to combination frequencies, or to other causes. In any case these lines will be much weaker than the fundamentals. In this type of molecule

TABLE 8
Inorganic solutions (type XO₃)

| SUBSTANCE | CONCENTRATION | RAMAN SHIFTS* | REFERENCES |
|--|---------------|---|-------------------|
| NaNO ₂ | Saturated | 588 _w 655 715 814 _w | (231) |
| NaNO ₂ | | 1220 1324 _s | (116) |
| NaNO ₂ | | 785 | 2151? |
| NaNO ₂ | | 815 | 1303 _s |
| KNO ₂ | | 1241 1326 _s | (191) |
| C ₃ (NO ₂) ₂ | | 1208 1321 _s | (231) |
| B ₃ (NO ₂) ₂ | | 1231 1327 _s | (231) |
| NaBO ₂ | | 1325 _s | (231) |
| NaH ₂ PO ₂ | | 952 1080 _w | (199) |
| H ₂ O ₂ | | 253 875 _s 903 | (199) |
| | | 1403 _m | (259) |

* The relative intensities are indicated by subscript letters following the numerical values of the Raman shifts: s = strong, m = medium, w = weak. The lack of any such designation indicates either that the line is faint or that there are no comparative data available in regard to the intensities. When the compound has been investigated by more than one observer, the shifts given do not usually represent the average value, but are preferentially selected from the more exact experimental determinations. In the case of considerable disagreement among observers the differing Raman shifts are generally included in parentheses.

TABLE 9
Inorganic solutions (type XO₃)

| SUBSTANCE | CONCENTRATION | RAMAN SHIFTS* | REFERENCES |
|--|---------------|----------------------|------------|
| NaClO ₃ | 51 per cent | 479 _w 611 | (196) |
| Mg(ClO ₃) ₂ | Saturated | 376? 533 604 | (254, 256) |
| NaBrO ₃ | 26 per cent | 367 _w | (196) |
| KIO ₃ | | 810 _m | (208) |
| KHSO ₃ | | 806 | (212) |
| H ₂ SeO ₃ | | 339 852 | (212) |
| N ₂ AsO ₃ | | 695 885 | (199) |
| NaVO ₃ | 144 203 | | (199) |
| Na ₂ PO ₃ | 228 367 | | (199) |
| Na ₂ H ₂ PO ₃ | | 642 _s | (199) |
| Na ₂ HPO ₃ | | 883 | (199) |
| | | 925 980 1030 | (199) |
| | | 1137 | |
| | | 1068 _s | |

* See footnote to table 8.

the shift at $\Delta\bar{\nu}$ 1325 in the case of nitrites is an inactive frequency due to symmetrical vibrations. Ghosh and Das (199) have attributed $\Delta\bar{\nu}$ 1403 for NaBO_2 and $\Delta\bar{\nu}$ 1080 for P(OH)_2 also to this type of vibration. In both the latter instances, however, the third fundamental was not obtainable. The frequency shifts, however, increase in proportion to the increased mass of the central atom in the order, boron, nitrogen, phosphorus. While hydrogen peroxide is not a molecule of this type, the appearance of a strong line at $\Delta\bar{\nu}$ 875 is indicative of the oscillation of the two oxygens against each other, differing widely from the O—O vibration in O_2 . This has not been studied sufficiently, however, to permit forming a definite opinion regarding the linearity or non-linearity of the molecule.

B. TYPE XO_3

Krishnamurti (134) considers that for the crystalline chlorates, iodates, and bromates the molecular configuration is somewhat similar to that ascribed to ammonia by Dennison (26). This molecule was considered as a symmetrical tetrahedron with nitrogen at the apex. All four frequencies in the case of chlorates, bromates, and iodates are active. The intensities of the lines increase in the order of chlorine, bromine, and iodine. The strongest frequency is that which occurs between $\Delta\bar{\nu}$ 800 and 950, depending upon the compounds studied. This is attributed to the displacement of the central atom away from the plane of the oxygen atoms. The essential difference between the spectra from the crystals and those obtained from the solutions is that the strongest frequency shift in the case of a crystal is made up of several components, but in a solution gives a single broad line which represents an average of these values. The splitting up of this frequency shift into several parts in going from solution to crystal is essentially attributable to the distortion of the XO_3 group produced by the field of neighboring cations.

The Raman spectra studies with the remaining compounds given in table 9 are admittedly incomplete. There is, apparently, however, a real difference between the spectrum obtained from H_2SeO_3 and that from KHSeO_3 and among those compounds

each of which contains a PO_3 group. So far as the evidence thus far obtained can be used as a criterion, the hydrogen in NaH_2PO_3 and Na_2HPO_3 cannot be linked directly to the phosphorus atoms. If this were the case, the line corresponding to this linkage would undoubtedly fall between $\Delta\bar{\nu}$ 2400 and $\Delta\bar{\nu}$ 2700. The characteristic H—S vibration in a solution of NaHS is $\Delta\bar{\nu}$ 2575. It is unlikely that a change from H—P to H—S would be of a different order of magnitude. By adding sodium hydroxide to a metavanadate solution, one can follow the progressive change of the metavanadate to the orthovanadate structure (199).

Nitrates

As has been previously stated, it is believed that the configuration of the nitrate ion is triangular, with the nitrogen in the center of the equilateral triangle. The most intense oscillation, $\Delta\bar{\nu}$ 1048, corresponds to the symmetrical expansion and contraction of the NO_3 group as a whole. Two other characteristic oscillations, $\Delta\bar{\nu}$ 726 and $\Delta\bar{\nu}$ 1357, are active vibrations. It was originally believed that these three frequencies in solution were independent of the cation and that the entire Raman spectrum was fairly simple (251). Subsequently, however, it has been observed by Grassmann (238, 239) and Nisi (148) that the intensity and magnitude of the shifts are a function both of the cation and the concentration of the solution. The frequency shifts obtained for various nitrates are given in table 10. Grassmann considers that $\Delta\bar{\nu}$ 720 to 730, which appear as a single line for the alkali nitrates, are split up into two components in calcium and cadmium nitrates, for example. In 8 *N* solutions these are of equal intensity. In 16 *N* solutions the $\Delta\bar{\nu}$ 741 line is stronger, and in 4 *N* solutions $\Delta\bar{\nu}$ 716 is the stronger. The shifts averaging $\Delta\bar{\nu}$ 720 are completely depolarized, while $\Delta\bar{\nu}$ 1048 is polarized. Nisi observed for the crystalline alkali nitrates a total change of 16 wave numbers proceeding from one end of the series to the other in the shift at approximately $\Delta\bar{\nu}$ 1048. There is a similar but much less pronounced change in the solutions of these salts, which would apparently indicate either an incomplete dissociation or an influence on the normal anion vibrations by the dissociated cations.

TABLE 10
Inorganic solutions (nitrates)

| SUBSTANCE | CONCENTRATION | RAMAN SHEETS* | | REFERENCES |
|---|----------------------------|--|---------------|---|
| LiNO ₃ | 14 N | 1050 _s | | (120, 238, 239) |
| NaNO ₃ | 33 per cent | 721 _w 1049 _s , 1361 _w (1389) | 1414 1663 | (120, 251, 239, 196, 191, 148, 225, 164, 243, 257, 240, 116) (251, 148, 243) |
| KNO ₃ | Saturated (20 per cent) | 730 _w 1049 _s , 1357 _w | 1413 1659 | |
| RbNO ₃ | 20 per cent | 1048 _s | | (148) |
| CsNO ₃ | 20 per cent | 1046 _s | | (148) |
| NH ₄ NO ₃ | 64 per cent | 728 _w 1050 _s , 1332 _w | 1400 1659 | (116, 234, 196, 251, 255, 243, 148, 164) |
| Cu(NO ₃) ₂ | | 279 442 717 _m -754 _w 1048 _s , 1325 _w -1421 | 1476 1654 | (184, 238) |
| AgNO ₃ | 3 N | 1041 _s | | (238, 239) |
| Be(NO ₃) ₂ | 8 N | 1049 _s | | (258) |
| CdNO ₃ | 3 N | 716 _w 741 _w 1047 _s | | (238, 243, 239, 240) |
| Mg(NO ₃) ₂ | 3 N | 1049 _s , 1346-1427 | (1655) (1811) | (258, 254, 256) |
| Ca(NO ₃) ₂ | Saturated | 721 716 _w -741 _m 1050 _s , 1349-1441 | 1647 (1811) | (196, 251, 258, 238, 148, 184, 256, 239, 240) |
| Sr(NO ₃) ₂ | Saturated | 728 _w 1049 _s , 1354 _w | | (251, 258) |
| Ba(NO ₃) ₂ | Saturated | 720 _w 1049 _s , 1350 _w | | (251) |
| Zn(NO ₃) ₂ | 3 N | 1047 _s | | (238, 258) |
| Al(NO ₃) ₃ | 3 N | 1049 _s | | (258) |
| Pb(NO ₃) ₂ | Saturated | 730 _w 1047 _s | | (251, 238, 239, 243) |
| Bi(NO ₃) ₃ | | 730 _w 980 1036 _s , (1236) 1417 _w | | (211) |

* See footnote to table 8.

This effect, however, is very close to the limit of accurate measurement of the wave-number shifts.

Silveira (184) also has observed a splitting in calcium nitrate of the $\Delta\bar{\nu}$ 720 shift to $\Delta\bar{\nu}$ 716 and 742, of which the latter is stronger. Similar behavior was observed in copper nitrate. In this case, however, $\Delta\bar{\nu}$ 717 was the more intense. There exists, furthermore, a second degeneracy of the average frequency, $\Delta\bar{\nu}$ 1357, in both of these compounds. This is split into two components, $\Delta\bar{\nu}$ 1325 and $\Delta\bar{\nu}$ 1421 for copper nitrate and $\Delta\bar{\nu}$ 1349 and $\Delta\bar{\nu}$ 1441 for calcium nitrate. No explanation is given for $\Delta\bar{\nu}$ 376 and 729. Silveira and Bauer (256) have observed a very feeble Raman shift at $\Delta\bar{\nu}$ 1811 for magnesium nitrate and calcium nitrate, for which there is equally no obvious explanation. The frequency shift at approximately $\Delta\bar{\nu}$ 1650 has been ascribed both to water (184) and to the nitrate ion (148). This band is very feeble and apparently appears in sulfate, chloride, or nitrate solutions. It is not, however, present in pure liquid water. Silveira and Bauer (256) attribute this band to a coupling between the ions and the molecules of water. This perturbation by water molecules is also held partially responsible for the doubling of the two degenerate frequencies of the nitrate ion. Unfortunately, however, $\Delta\bar{\nu}$ 1650 falls in a region very close to the water band excited by the 4047 A.U. mercury line. This adds to the confusion as to the real existence of this frequency shift—Silveira and Bauer notwithstanding. However, it may be again mentioned that one of the fundamentals to be expected from the water molecule according to Johnston and Walker (169) is $\Delta\bar{\nu}$ 1648, which does actually appear in the vapor state, but which apparently is completely absent in pure liquid water. Silveira (254) originally noted this shift in magnesium chloride and magnesium nitrate solutions but not in solutions of magnesium chlorate. It was first attributed to a probable hydrate formed by the magnesium ion.

Sterling and Laird (257) examined solutions of sodium nitrate at different concentrations, particularly with reference to the behavior of $\Delta\bar{\nu}$ 1049. No changes in this frequency shift were observed. It was presumed in highly concentrated solutions of

sodium nitrate that the sodium nitrate molecules would exist in sufficient concentration to give a somewhat different spectrum than would be obtained from the nitrate ions alone.

Solutions of bismuth nitrate in nitric acid are highly complex, according to Ollano (211). This salt is hydrolyzed even in the presence of nitric acid. In addition to $\Delta\bar{\nu}$ 1414, 1032, and 720, $\Delta\bar{\nu}$ 980 was observed and attributed to the fourth fundamental frequency of the nitrate ion. $\Delta\bar{\nu}$ 1236 is doubtful. In addition to this, $\Delta\bar{\nu}$ 1600 and $\Delta\bar{\nu}$ 1500 observed were attributed to hydrolyzed bismuth, as previously discussed in the Raman effect of bases. The nitrates of lanthanum, cerium, and thorium have also been investigated (164).

TABLE 11
Inorganic solutions (carbonates)

| SUBSTANCE | CONCENTRATION | RAMAN SHIFTS | REFERENCES |
|---------------------------------------|---------------|--------------|---------------------------|
| Na ₂ CO ₃ | 1 N | 1065 | (117, 166) |
| K ₂ CO ₃ | 1 N | 1067 (1075) | (117, 129, 196, 166, 244) |
| KHCO ₃ | 26 per cent | 1035 | (196) |

Carbonates

Embirikos (117) observed that in 1 N and 2 N aqueous solutions the frequency shift of the alkali carbonates corresponding to the inactive vibration is slightly less in solution than in crystals.

The configuration of the carbonate ion approximates that of the nitrate ion. Only the shift corresponding to the symmetrical oscillation has been recorded so far. These are given in table 11. This shift is appreciably lower in the acid carbonate than in the carbonate. The lines characteristic of carbon dioxide gas have no counterpart in these solutions. As is to be expected, there is no shift corresponding to the C—H vibration.

The sulfites will be discussed under the sulfur compounds, table 14.

C. TYPE XO₄

The Raman shifts given in table 12 for a variety of compounds of the general type XO₄ are admittedly incomplete. Nor are the

TABLE 12
Inorganic solutions (type XO₄)

| SUBSTANCE | CONCENTRATION | RAMAN SHIFTS* | | REFERENCES |
|--|---------------|------------------------|---|-----------------|
| NaH ₂ PO ₄ | 38 per cent | 358 | 518 _m | (208) |
| Na ₃ VO ₄ | 14 | | 889 _s 1061 _m | (208, 199) |
| Na ₂ CrO ₄ | 13 | | 875 (907) | (208) |
| Na ₂ WO ₄ | | 371 _w | 855 _m 931 _w 1017 1394 1540 _w | (208, 199, 233) |
| Na ₂ MoO ₄ | 17 | 330 _m (314) | 845 _m 898 _s | (208, 233) |
| Na ₂ SeO ₄ | 17 | 335 432 | 830 _s | (208) |
| Na ₃ AsO ₄ | 7 | 349 462 _w | 837 | (208, 199) |
| K ₂ WO ₄ | 26 | | 933 _s | (208) |
| (NH ₄) ₂ MoO ₄ | | 256 356 | 885 _w 938 _s | (208, 199) |
| H ₂ TeO ₆ | 15 | | 648 _m | (208) |

* See footnote to table 8.

estimates of relative intensities very accurate. The individual differences in similar compounds which may exist in two forms, such as, for example, sodium arsenite and sodium arsenate, are strikingly marked. The progressive change from the metavanadate to orthovanadate structure has already been mentioned. In addition, Ghosh and Das (199) point out that the neutralization of an alkaline solution of the sodium tungstate causes a marked decrease in the intensity of the Raman spectrum obtained from this compound. No lines were observed for silicic or molybdic acids. Nisi (208) observed that the principal Raman frequency shifts for compounds of the type Na_2SO_4 , Na_2SeO_4 , and H_6TeO_6 decrease with increasing atomic number. The respective principal shifts for these three compounds are $\Delta\bar{\nu}$ 979, 830, and 648. On the contrary, however, compounds of the type Na_2CrO_4 , Na_2MoO_4 , and Na_2WO_4 show increasing wave-number shifts with increasing atomic number, the respective principal $\Delta\bar{\nu}$ being 855, 898, and 931. Nisi ascribed this contradiction to a different distribution of extranuclear electrons, the mode of binding of the central atoms to the surrounding oxygen atoms being different for the two groups.

The solution of NaH_2PO_4 gives one strong line which nearly coincides with that due to the H_2PO_4 group, obtained from the ionization of H_3PO_4 . No lines could be observed in a solution of Na_3PO_4 .

Sulfates

The average fundamental frequency shifts for the sulfate ion observed by Ramaswamy (251) are $\Delta\bar{\nu}$ 457, 617, 981 and 1102, of which the first and third are inactive and the other two are active frequencies. The solutions studied comprise the sulfates of sodium, potassium, ammonium, magnesium, zinc, cadmium, and aluminum. Within the limits of the accuracy of measuring these frequency shifts, no definite changes were observed with different cations, in contrast to the observations with crystalline sulfates. On the whole, the magnitudes of the displacement are slightly less than those observed with crystals. Krishnamurti (133) observed that a saturated solution of ferrous sulfate gives

the $\Delta\bar{\nu}$ 980 shift in the usual position, in contradistinction to his observation for the crystalline ferrous sulfate, where it was weak or entirely absent. As has been pointed out previously, the observation with respect to the crystals is open to doubt. The average frequency shifts for the SO_4 ion, as indicated above, have been confirmed by Fadda (198).

Embirikos (117) investigated the effect of concentration on the shift approximately represented by $\Delta\bar{\nu}$ 980. There is certainly a diminution in the magnitude of the shift in going from crystal to solution. Crystalline lithium sulfate, for example, gives $\Delta\bar{\nu}$ 1003, a 1 *N* solution of the same compound, $\Delta\bar{\nu}$ 989, and a 2 *N* solution, $\Delta\bar{\nu}$ 999. As the crystalline compound, however, becomes more hydrated, the magnitude of the frequency displacement becomes less, and more nearly comparable with that of a fairly dilute solution. The crystalline compound, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, gives $\Delta\bar{\nu}$ 987. A 1 *N* solution of MgSO_4 yields $\Delta\bar{\nu}$ 986, and a 2 *N* solution, $\Delta\bar{\nu}$ 996. The average value for the dilute solutions of all the compounds studied is slightly greater than those observed by Ramaswamy (251). This seems to be without significance, and may be due to a systematic difference in measurement. While there is a noticeable increase in the magnitude of this displacement with increasing concentration, the amount of this increase is reasonably uniform, being approximately ten wave numbers. Under ordinary conditions of measurement the reproducibility is usually not less than five wave numbers. The higher frequency shifts appearing in ammonium sulfate are attributable to the ammonium group rather than the sulfate group (208, 255). Nisi (146) observed no essential difference in the magnitude of the frequency shifts for manganous sulfate at different concentrations, but did observe a slight increase in $\Delta\bar{\nu}$ 980 for the aqueous solution of ferrous sulfate as compared with the crystalline compound, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The results found with nickel sulfate would indicate a slight decrease, amounting to approximately five wave numbers for the solution as compared with the crystalline $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.

It must be reiterated that these slight differences, except in cases where such observations are the main subject of experiment, are not to be given too much weight.

TABLE 13
Inorganic solutions (sulfates)

| SUBSTANCE | CONCENTRATION | KAMAN SHIFTS* | REFERENCES |
|--|----------------|---------------------------|-------------------------------------|
| Li ₂ SO ₄ | 18 per cent | 442 593 | (208, 117, 218) |
| Na ₂ SO ₄ | Saturated | 460 _m 615 | (251, 117, 198, 208, 247, 219) |
| K ₂ SO ₄ | Saturated | 457 _m 619 | (251, 208) |
| (NH ₄) ₂ SO ₄ | | 454 _m 618 | (117, 251, 184, 208, 255, 212, 196) |
| K ₂ Al ₂ (SO ₄) ₄ | | 477 607 | (241, 125, 146, 127) |
| CuSO ₄ | | 279? 429 610 _m | (247, 241, 184, 146, 127, 244, 233) |
| MgSO ₄ | | 456 _m 617 | (247, 208, 218, 251, 117, 127) |
| BcSO ₄ | | 442 _m 613 | (146) |
| ZnSO ₄ | | 454 _m 620 | (208, 251, 117) |
| CdSO ₄ | | 451 _m 621 | (208, 251, 117) |
| Al ₂ (SO ₄) ₃ | | 457 _m 614 | (247, 251) |
| MnSO ₄ | 1 N | 452 _m 613 | (117, 218, 146) |
| FeSO ₄ | 3 M, Saturated | 673 | (133, 95) |
| NiSO ₄ | | 980. | (146) |

* See footnote to table 8.

Silveira (184) observed several new lines in the Raman spectrum of copper sulfate, which is apparently more complex than the other sulfates. $\Delta\bar{\nu}$ 1110 apparently has two other adjacent frequencies, the three composing a triplet. The shifts corresponding to $\Delta\bar{\nu}$ 1472 and 1665 are probably not attributable to the copper sulfate. The doublet $\Delta\bar{\nu}$ 717 and 754 has been recorded as a single line by Hollaender and Williams (127) at $\Delta\bar{\nu}$ 723. The tendency to the splitting of frequencies in copper sulfate into doublets and triplets is particularly noticeable in the crystal (146), but was not observed by him in solutions of copper sulfate.

Sulfur compounds

The constitution of some of the complex compounds of sulfur in solution may be at least partially determined by using the same method of approach as that employed with the acids. The data upon which such an analysis may be predicated are given in table 14. On first inspection, it is apparent that there are certain similarities in the spectra of these substances, but it is also equally evident that there are many dissimilarities, and a detailed analysis is necessary to correlate the results.

To begin with, however, it may be pertinent, in order to make the picture more complete, to record the characteristic shifts of liquid SO_2 , SO_3 , and S_2O_6 . For SO_2 , the average values, $\Delta\bar{\nu}$ 525, 1145, and 1340 are obtained (197, 209, 226, 227, 232). Of these three shifts the central one is by far the strongest. For SO_3 , $\Delta\bar{\nu}$ 535, 1068, and 1403 are observed (12, 226, 227). To S_2O_6 , Bhagavantam (226, 227) attributes $\Delta\bar{\nu}$ 290, 370, 666, 697, 1271, and 1489. It is not to be expected that the SO_3 ion will give a spectrum identical with that of SO_3 liquid or SO_3 gas. There is naturally a greater dissimilarity between the uncharged gas and the SO_3 ion than there is between such an ion in the crystal lattice and such an ion in solution.

The early attempts to determine the Raman spectra characteristic of the sulfite ion led only to the distinguishing of the relatively strong line (208) at $\Delta\bar{\nu}$ 968. This is appreciably lower than that observed by Dickinson and Dillon (196) at $\Delta\bar{\nu}$ 988. Fadda (198) assigned $\Delta\bar{\nu}$ 471, 602, and 984, all of which fall re-

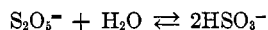
markably close to the frequencies observed for the sulfates with the exception of the shift $\Delta\bar{\nu}$ 1110, which was absent.

As has been discussed under the Raman spectra of acids, an aqueous solution of sulfur dioxide gives the spectrum of sulfur dioxide rather than sulfurous acid. The sodium sulfite solutions, however, show no similarity to this behavior.

The existence of the ion HSO_3 is subject to some dispute. Ghosh and Das (199) assign the frequencies $\Delta\bar{\nu}$ 346, 826, 963, and 1406 to this ion in a solution of NaHSO_3 . As has been previously mentioned, this ion is probably not present in sulfurous acid, although Nisi (209) tentatively assigned $\Delta\bar{\nu}$ 1054 to the HSO_3 ion and 1017 to the SO_3 ion, observed in the sulfurous acid solutions. The latter, together with the tentative assignment of $\Delta\bar{\nu}$ 1199 by Fadda to HSO_3 , are probably erroneous.

Foerster, Brosche, and Norberg-Schulz (237) have determined the non-existence of the acid sulfites of sodium and potassium in the solid state, although there is a crystalline double salt corresponding to $\text{K}_2\text{S}_2\text{O}_5 \cdot 4\text{KHSO}_3$.

Before considering HSO_3 ions further, it may be pointed out that they can be formed (237, 245) according to the equation,



and hence are somewhat intimately connected with the Raman spectrum of S_2O_5 ions.

It is the contention of Fadda (236) that NaHSO_3 does not exist in solution, the Raman spectrum of this compound indicating only the presence of S_2O_5 ions. Nisi (208) determined the Raman spectrum of a 17 per cent solution of $\text{Na}_2\text{S}_2\text{O}_5$ and obtained $\Delta\bar{\nu}$ 236 (s), 426 (m), 571 (w), 652 (m), 1015 (w), and 1054 (s), where s stands for strong, m for medium, and w for weak. Fadda obtained for a solution of supposed NaHSO_3 , prepared according to the method of Muspratt (248, 249), $\Delta\bar{\nu}$ 242 (vs), 420 (m), 656 (s), and 1009 (vs). It is to be noted that $\Delta\bar{\nu}$ (427), 593, (978), and 1048 are present in the spectrum of KHSO_4 (208, 225). It is the contention of Fadda, therefore, that the $\Delta\bar{\nu}$ 571 and 1054 shifts observed by Nisi in $\text{Na}_2\text{S}_2\text{O}_5$ in reality owe their origin to the presence of HSO_4^- . To prove

TABLE 14
Inorganic solutions (sulfur compounds)

| SUBSTANCE | CONCENTRATION | RAMAN SHIFTS* | | | | | REFERENCES |
|---|------------------------------|------------------|------------------------|------------------|---------------------|--------------------------|-----------------|
| KHSO ₄ | { 12 per cent 28 per cent | 427 | 593 | 978 _m | 1048 _s | | (208, 225) |
| NaHSO ₃ ?..... | | (314) 346 | | 826 | 963 | 1406 | (236, 199) |
| Na ₂ SO ₃ | 16 per cent | | | 968 _m | | | (208) |
| Na ₂ SO ₃ | Saturated | 471 | 602 | 984 _m | | | (198) |
| K ₂ SO ₃ | 52 per cent | | | 988 _m | | | (196) |
| K ₂ SO ₃ | 20 per cent | | | 968 _m | | | (208) |
| Na ₂ S ₂ O ₃ | | 335 | 448 _s | 543 | 665 | (1078) 1129 _m | (212, 146, 208) |
| Na ₂ S ₂ O ₄ | 17 per cent | 407 | 458 | 983 _m | 1057 _m | | (208) |
| Na ₂ S ₂ O ₅ | 17 per cent | 236 _s | 426 _m | 1015 | (1054) _s | | (208, 236) |
| Na ₂ S ₂ O ₆ | Saturated | 279 | (571) 652 _m | 709 _m | 1090 _s | | (212) |
| K ₂ S ₂ O ₇ | 12 per cent | | 585 | 980 | 1052 _m | | (208) |
| (NH ₄) ₂ S ₂ O ₈ | 25 per cent | 216 | 322 | 836 | 971 | 1027 | 1290 |
| Na ₂ S ₂ O ₈ | | | | 833 _m | | | (199) |
| NaHS..... | | | | | | 2575 _s | (199) |

* See footnote to table 8.

this point the experiments were carried out without contact with air. The solution showed no test for sulfate before or after experiment. No traces of $\Delta\bar{\nu}$ 571 or 1054 were observable. This leaves then a reasonably good agreement between the Raman spectra of $\text{Na}_2\text{S}_2\text{O}_5$ (as determined by Nisi with these corrections) and supposed NaHSO_3 , the logical conclusion being the non-existence of NaHSO_3 in solution. There is, however, one factor which should be mentioned, namely, if $\Delta\bar{\nu}$ 1054 observed in the spectrum of $\text{Na}_2\text{S}_2\text{O}_5$ is to be attributed to air oxidation, then the inevitable conclusion is that Nisi's solution must have been largely oxidized, since this was the strongest line observed by him. In addition to the frequencies given, for the S_2O_5 ion, Fadda observed $\Delta\bar{\nu}$ 314 in a 50 per cent solution, but this was absent in a 17 per cent solution. This was attributed to a polymer of $\text{Na}_2\text{S}_2\text{O}_5$. In addition, $\Delta\bar{\nu}$ 1142, characteristic of sulfur dioxide, was also present. These results are not compatible with those of Ghosh and Das (199).

The next more complicated compound in the series is $\text{Na}_2\text{S}_2\text{O}_3$. The similarity between the spectrum of this compound and that of the sulfates is marked. This is most reasonably explicable on the assumption that the S_2O_3 ion has a constitution similar to the sulfates, that is, with one oxygen replaced by a sulfur atom and the other oxygen atoms being bound to one sulfur atom only. These results may be compared with the shifts observed by Nisi (146) for crystalline $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. These were $\Delta\bar{\nu}$ 324, 433 (s), 546, 612, 674, 1018, 1116, and 1162. With allowance for possible lattice frequencies and the tendency to split frequencies in crystals, the results, as compared with those obtained from solutions, are reasonably compatible. Each of the lines corresponding to the two active vibrations clearly splits into more than one component. The relative intensities, however, of the inactive vibrations for S_2O_3 are the reverse of those which exist in the case of the sulfates.

According to Pringsheim and Yost (212) for the S_2O_3 ion the oxygen atoms are symmetrically arranged in respect to each sulfur atom, giving the formula $\text{O}_3\text{S}-\text{SO}_3$. It may be mentioned that the characteristic frequency of the $\text{S}-\text{S}$ vibration in the

organic disulfides, such as methyl disulfide, occurs (260) at $\Delta\bar{\nu}$ 512, for which there is no counterpart in the S_2O_6 ion.

The compound $Na_2S_2O_4$ can be equally well written $NaSO_2$. In the presence of water only slightly above room temperatures it may be converted into $Na_2S_2O_3$ and $NaHSO_3$. The Raman spectrum is not consistent with the formula $NaSO_2$ since the dissociation of this compound would lead to a spectrum more similar to that of SO_2 than the one observed. From an analogy of the similarity of the spectrum with that of the sulfates, it might be presumed that the oxygens are attached to one rather than both sulfur atoms.

The compound $K_2S_2O_7$ in solution gives, according to Nisi (208), a Raman spectrum which nearly coincides with that given by $KHSO_4$. This is not surprising when one considers that $K_2S_2O_7$ is obtained by dehydrating two molecules of $KHSO_4$, and probably results, on solution, in the formation of HSO_4 ions.

Compounds of the type giving S_2O_3 ions have been insufficiently studied as yet from the point of view of Raman spectra to provide more than a basis for pure speculation.

Nisi (209) has attempted to determine the characteristic frequency vibrations of the SO_2 and SO groups from the spectrum of the organic sulfonic acids, chlorosulfonic acid, sulfonyl chloride, sulfur oxychloride, and organic sulfites. He concluded that at least one line between $\Delta\bar{\nu}$ 1130 and 1190 was characteristic of the SO_2 group in the combination and that possibly $\Delta\bar{\nu}$ 1220 was characteristic of the SO group.

It is difficult to correlate these conclusions with the other data. The organic derivatives, such as benzenesulfonic acid, have sufficiently complicated spectra themselves, and the assignment of a specific frequency to a specific group is increasingly difficult. Since the molecular species in acids will vary with dilution, it is also precarious to use these substances as standards.

In summarizing, it may be stated that these Raman spectra studies, while as yet in most cases incomplete, provide a fair amount of information concerning the constitution of complex sulfur compounds in solution. Salts of the type $R-SO_3$, unlike the acids, have a definite constitution and configuration. The

existence of an acid sulfite in solution is an open question. It is possible that the compound exists as $S_2O_5^-$ rather than HSO_3^- . On the contrary, salts of the type $K_2S_2O_7$ in solution may exist as HSO_4 ions. Certainly the binding force between the sulfur and the oxygen atoms in all of the compounds is of the same order, and the ionization of the HSO_4 ion to SO_4 is likewise indicated. To compounds giving ions of the type S_2O_3 , S_2O_4 , and S_2O_6 , from symmetry considerations and their similarities and dissimilarities to sulfates, can be ascribed a fairly reasonable constitution.

These compounds have not been investigated and reinvestigated by different observers. In time a clearer and more accurate picture will undoubtedly be obtainable. It must not be forgotten that partially, at least, such interpretations are predicated on analogies and extrapolations. Often these may be accepted as factual and can be considered reasonably accurate. In the case of the sulfur compounds, however, accurate fundamental information concerning them from the point of view of inorganic chemistry is meagre. In any case, whatever interpretation may be ultimately accepted, the data obtained from the point of view of Raman spectra must be quantitatively accounted for.

Perchlorates

Since the mass of the chlorine and the configuration of the chlorate ion are approximately identical with those of the sulfate ion, the Raman shifts should closely approximate those obtained for the sulfates provided the binding force between the oxygen and sulfur is nearly the same as that between chlorine and sulfur. It can be seen from table 15 that this is the case. The strongest shift, averaging $\Delta\bar{\nu}$ 934, is approximately fifty wave numbers less than the equivalent displacement observed with the sulfates. Ollano (210) observed two large frequency shifts at $\Delta\bar{\nu}$ 3544 and 3599. The former he attributed to H_3O^+ and the latter to $H(H_2O)_n^+$.

For KIO_4 $\Delta\bar{\nu}$ 702 probably represents the inactive frequency and is shifted considerably lower, owing to the increased mass of the iodine atom.

TABLE 15
Inorganic solutions (perchlorates)

| SUBSTANCE | CONCENTRATION | RAMAN SHIFTS* | REFERENCES |
|--|------------------------|--|------------|
| | <i>moles per liter</i> | | |
| NaClO ₄ | 10.8 | 463 _w 626 _w 935 _s 1120 _w | (177, 210) |
| KClO ₄ | 0.14 | 461 632 936 _s | (177, 210) |
| NH ₄ ClO ₄ | 1.9 | 463 626 930 _s 1109 | (177, 210) |
| KIO ₄ | | 702 _m | (208) |

* See footnote to table 8.

Halogens

In table 16 are given the Raman frequency shifts observed for polyatomic halogen derivatives. Those halogen derivatives which occur as liquids will be considered separately. Those compounds which ionize completely in solution give no Raman lines which may be attributed to an anion-to-cation oscillation. The large frequency shifts from $\Delta\bar{\nu}$ 1600 upwards (if real) are presumably due to perturbations between the ions and water, as previously discussed. Cadmium chloride shows evidence of homopolar binding in solutions, as do the chlorides of zinc, mercury, magnesium and bismuth. The $\Delta\bar{\nu}$ given for ammonium chloride may be associated with the NH₄ group. A progressive decrease in the magnitudes of the shifts for the chlorine, bromine, and iodine derivatives of mercury is attributable to the increased mass of the respective anions.

A concentrated solution of mercuric chloride in methyl alcohol gives a shift at approximately $\Delta\bar{\nu}$ 275 according to Krishnamurti (132), or in practically the same position as that observed in the crystals but considerably broadened. Crystalline zinc chloride was also observed to give a faint line at $\Delta\bar{\nu}$ 234. Unlike mercuric chloride, which was considered to be a linear model by Krishnamurti, zinc chloride was presumed to be triangular.

Aqueous solutions of zinc chloride were investigated by Hibben (125) over a hundredfold concentration range. With concentrated solutions $\Delta\bar{\nu}$ 297 and 396 were observed, the former shift having an intensity approximately six times greater than the latter. Between concentrations of 11 molal and 1 molal these

TABLE 16
Inorganic solutions (halides)

| SUBSTANCE | RAMAN SHIFTS* | REFERENCES |
|-------------------|---------------------------------------|---------------------------|
| K_2HgCl_4 | 266 | (229) |
| K_2HgBr_4 | 166 | (229) |
| K_2CdBr_4 | 160 | (230) |
| K_2HgI_4 | 126 | (229) |
| $KCdI_3$ | 118 _s | (229) |
| Na_2CdI_4 | 109 | (230) |
| $MgCl_2$ | 376 (350 - 785) | (254, 256) |
| NH_4Cl | 1115 1300 1453 | (255) |
| $HgCl_2$ | 320 | (136, 228, 261, 230, 225) |
| $HgBr_2$ | 205 | (228, 230) |
| HgI_2 | 150 | (229, 230) |
| $BiCl_3$ | 108 _s 242 289 _s | (235, 23, 111) |
| Al_2Cl_6 | 348 541 _m 808 _w | (125) |
| $ZnCl_2$ | 297 _w 396 _s | (125) |
| $LiCl$ | (1658) 1762 1811 | (256) |
| $CdCl_2$ | (133) 243 | (256, 230) |
| CdI_2 | 133 | (230) |
| $CaCl_2$ | (1651) | (256) |
| $SrCl_2$ | (1650) | (256) |

* See footnote to table 8.

relative intensities remain approximately the same, although there is a sharpening of both lines with dilution. With further dilution, however, the ratio of the intensity of $\Delta\bar{\nu}$ 297 to that of $\Delta\bar{\nu}$ 396 becomes much less, the two lines having approximately equal intensity at a concentration of half molal. There may also be other lines present in the very dilute solutions. If the stronger line is attributed to the linear oscillation of a chlorine atom against a ZnCl group and the weaker one is attributable to a chlorine atom oscillating against a zinc atom in a ZnCl ion, then this behavior is reasonably explicable since the more concentrated solution consists largely of undissociated zinc chloride and the more dilute solution has a higher concentration of the ZnCl ion. This is in agreement with the stepwise dissociation of zinc chloride as determined by conductivity measurements (242, 250, 252).

Aqueous solutions of Al_2Cl_6 give $\Delta\bar{\nu}$ 348, 541, and 808, the middle shift being the strongest, according to Hibben (125). The latter two of these are identical with the shifts obtained from anhydrous Al_2Cl_6 crystals, $\Delta\bar{\nu}$ 348 being indeterminable in the crystalline material. It is presumed from this that Al_2Cl_6 exists in aqueous solution in the polymerized form. From the point of view of inorganic chemistry its structure is open to question (246). Sidgwick considers (253) that the AlCl_3 molecules are coupled through two chlorine atoms by coordination. The relative simplicity of the spectrum would argue in favor of a symmetrical arrangement. Hydrated Al_2Cl_6 shows no Raman lines comparable with the anhydrous material, which is reasonable if one views the aluminum atom in this case as surrounded by water molecules, as has been shown to be the structure of some of the chlorides (262).

SUMMARY

The Raman spectra of solutions give frequency shifts corresponding to both solute and solvent. The frequency displacements of the solute are essentially those observed for crystals. When, however, the solute ionizes, only those Raman shifts are present which correspond to the polyatomic ion. If ionization

takes place in successive stages, this is indicated. The so-called lattice vibrations observed in crystals are missing in solutions. The cation, however, is not without some influence in solution, but it is much less than that observed in crystals. The influence of the cation is further indicated by the occasional marked change in the Raman spectrum in passing from the salt to the acid form. The spectra observed from compounds containing the same anion but different cations are sometimes appreciably different. The change from the alkalis to the alkaline earths, for example, produces a much more complicated spectrum.

The frequency shifts corresponding to the symmetrical vibrations in an ion are appreciably less in solution than in the crystals. This would indicate a slight diminution of the force exerted between the atoms. The spacial configurations of the ions are somewhat analogous in gases of the same general type. Changes in valency produce marked changes in the Raman spectra of the respective compounds. The relative intensities of the lines vary with changing concentrations. The inactive shift for sulfate solutions more nearly approaches that of the crystal with increased concentration. Indeed, the displacement in a concentrated solution may exceed that of the corresponding crystal if the latter is highly hydrated. The similarity in spacial arrangement and in binding force between similar ions is marked. The polymerized form of certain crystals is sometimes retained in solution. The more complex sulfur compounds sometimes may retain the same form in solution as they possess in crystals or they may not do so, depending on the particular compound. If the material to be examined is sufficiently soluble, the Raman spectra of solutions offer a method of determining the constitution under conditions which often cannot be approached by any other means. Intermediate compounds and complex-compound formations in solution will be discussed in the succeeding section.

VIII. RAMAN SPECTRA OF COMPLEX-COMPOUND FORMATIONS

Complex compounds may exist in the vapor, liquid, or solid states of aggregation or in solution. By complex compound is meant those molecules, alike or unlike, which may combine to

form double polymers, mixtures, coördinated complexes, and quasi compounds, whose real existence has been more or less hypothetical. The Raman spectra method in many cases is a unique means of determining the existence of certain types of complexes. In true mixtures the Raman spectrum of each compound is approximately independent of others. If, however, there is an actual interaction, the normal Raman spectra will be considerably affected. A more or less classical example of this is in polymerization. This is evidenced, for example, in the polymerization of sulfur trioxide. Chemical evidence shows the presence of two varieties of sulfur trioxide, having a distinct melting point, one consisting of the polymerized molecules with the formula S_2O_6 , at low temperatures, and depolymerizing to SO_3 near $100^\circ C$. The Raman spectrum at room temperature consists of nine frequencies, according to Bhagavantam (226), which were attributed to the S_2O_6 molecule. On heating to approximately $100^\circ C$., six of these, namely, $\Delta\bar{\nu}$ 290, 370, 666, 697, 1271, and 1489, become considerably weaker, and the remaining three, $\Delta\bar{\nu}$ 535, 1068, and 1489, become distinctly stronger. The latter three frequencies are attributed to SO_3 . This process is perfectly reversible, and may be repeated with identical results. Thus, polymerization of SO_3 and the depolymerization of S_2O_6 can be followed by means of the Raman spectrum of the components of this mixture.

In the solid state the Raman spectrum from the solid eutectic of $NaNO_3 + KNO_3$ shows only one sharp principal frequency for the NO_3 group when freshly prepared, according to Gerlach (264). After a period of approximately one day, however, the initially sharp line becomes gradually broad and diffuse, finally separating with increasing time into two sharp distinct lines, one having a frequency shift corresponding to that of sodium nitrate and the other to potassium nitrate. The initial sharp line obtained from the eutectic lies half-way between the two final lines attributed to sodium nitrate and potassium nitrate, respectively. X-ray diffraction patterns showed no difference between samples at different ages, and the results are independent of the rate of cooling. It might be mentioned, however, that

KNO_3 I first changes metastably to KNO_3 III, which then inverts to KNO_3 II, according to Kracek (266, 267). Whether or not this has any connection with the suppositions of Gerlach is a matter for further investigation.

Proof of the formation of mixed molecules by the use of the Raman effect has been demonstrated by Trumpy (270, 271). The procedure was first to determine the Raman shifts for pure compounds, such as phosphorus trichloride and phosphorus tribromide. These were then mixed with varying ratios and the Raman spectra of the mixtures determined. These mixtures

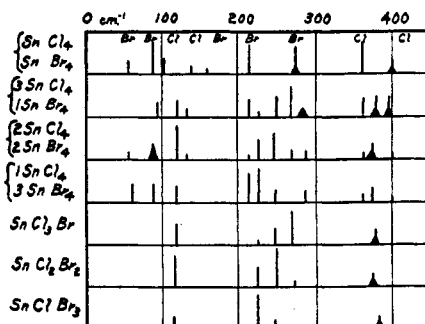


FIG. 16. RAMAN SPECTRA OF MIXED MOLECULES
(After Trumpy)

give rise to new Raman lines which change in intensity with the amount of each compound. With ratios of two parts phosphorus trichloride and one part phosphorus tribromide, and one part phosphorus trichloride and two parts phosphorus tribromide, the results showed two types of mixed molecules to be present, namely, PCl_2Br and PClBr_2 . The $\Delta\bar{\nu}$ found for phosphorus trichloride are $\Delta\bar{\nu}$ 190, 256, 485, 510, and for phosphorus tribromide, $\Delta\bar{\nu}$ 115, 161, 379, and 397, of which the lowest shifts are the strongest. Mixtures of silicon tetrabromide and stannic bromide showed no new lines. The system $\text{SnCl}_4\text{-PBr}_3$ shows the presence of SnBr_4 , PCl_3 , PClBr_2 , PCl_2Br , SnCl_3Br , SnCl_2Br_2 , SnClBr_3 . These results are given graphically in figure 16.

Krishnamurti (136) observed $\Delta\bar{\nu}$ 313 (s) and $\Delta\bar{\nu}$ 381 (w) for

mercuric chloride crystals. In solution, with one mole mercuric chloride and one mole ammonium chloride, were observed $\Delta\bar{\nu}$ 274 and $\Delta\bar{\nu}$ 313, both lines being broad and diffuse with the former stronger than the latter. With one mole mercuric chloride and two moles ammonium chloride only $\Delta\bar{\nu}$ 269 was observed. With crystalline $(\text{NH}_4)_2\text{HgCl}_4$ $\Delta\bar{\nu}$ 273 was obtained. With a mixture, therefore, of the composition $\text{HgCl}_2, 2\text{NH}_4\text{Cl}$, whether in solid state or in solution, a Raman line $\Delta\bar{\nu}$ 269 is observed, characteristic of the complex salt $(\text{NH}_4)_2\text{HgCl}_4$. Any mercuric chloride in excess of this composition gives its own line characteristic of mercuric chloride, namely, $\Delta\bar{\nu}$ 313, thus demonstrating the existence of this complex in solution. These results are quite similar to those obtained by Braune and Engelbrecht (228, 229) with solutions of mercuric halides and potassium chloride.

There is some evidence for the existence of solid inorganic polymers. Krishnamurti (130) attributes the existence of a faint Raman line, which appears in crystals of lithium, mercuric, and aluminum nitrates, and which is shifted between ten and twenty wave numbers from the strong inactive frequency, to the effect of polymerization of the molecule in a solid state. These faint components appear at $\Delta\bar{\nu}$ 1052 for lithium nitrate, $\Delta\bar{\nu}$ 1021 for mercuric nitrate, and $\Delta\bar{\nu}$ 1058 for aluminum nitrate. In the first two cases this appears on the shorter wave length side of the principal line, while with aluminum it appears on the opposite side. In the case of aluminum nitrate, the strong line is attributed to the polymerized molecule and the fainter line to the simple one. With lithium nitrate and mercuric nitrate the strong shift is attributed to the monomeric form and the weak to the dimeric. This component does not occur in concentrated solutions of lithium nitrate. In view of the subsequently observed splitting of Raman shifts in other compounds, due to degeneracy, it is not altogether certain that the explanation given by Krishnamurti would now be considered by him as the most probable one. The polymerization of aluminum chloride and esters of silicic acid has already been discussed (125, 159, 160).

The existence of complex compounds in solution is a particu-

larly interesting phase of Raman spectra investigation, which may be illustrated in the following examples. A solution of mercuric chloride in methyl alcohol gives $\Delta\bar{\nu}$ 319, which is considerably broadened in comparison with the shift $\Delta\bar{\nu}$ 313, observed in mercuric chloride crystals, but no obvious change was noted in the spectrum of methyl alcohol by Krishnamurti (136). Solutions of zinc chloride in methyl alcohol were observed by Hibben (125) to result in a modification of the methyl alcohol spectrum and apparently in a suppression of the normal zinc chloride lines. The time of exposure which normally brings out the characteristic shifts of zinc chloride in an aqueous solution or in ethyl alcohol solution, failed to elicit any lines for zinc chloride, in a methyl alcohol solution containing one mole of zinc chloride to two moles of methyl alcohol. So far as the alcohol is concerned, however, $\Delta\bar{\nu}$ 1036, characteristic of the $C\leftrightarrow OH$ was shifted to a lower value by twenty-two wave numbers, and $\Delta\bar{\nu}$ 2841 and 2945 were shifted to a higher value by twenty-three wave numbers. The most pronounced effect was the diminution in intensity of $\Delta\bar{\nu}$ 1472, characteristic of the transverse oscillation of $C\leftrightarrow H$. If the oscillation frequency of the zinc chloride were shifted considerably to a much lower frequency, the Raman line would not be observable on account of the general scattering of the exciting radiation. On the other hand, the effect of the interaction between zinc chloride and methyl alcohol may be to make less probable the normal transitions which give rise to the normal frequency shifts in zinc chloride. A somewhat similar and more pronounced effect was noted in alcoholic solutions of Al_2Cl_6 . In contrast to this behavior, solutions of zinc chloride in ethyl alcohol gave $\Delta\bar{\nu}$ 300 (s) and $\Delta\bar{\nu}$ 308 (w). The former shift is approximately that observed for zinc chloride in aqueous solution. However, $\Delta\bar{\nu}$ 308 was not observed in aqueous solution, and $\Delta\bar{\nu}$ 396, observed in aqueous solution, was missing. It may be reiterated that $\Delta\bar{\nu}$ 300 was attributed to un-ionized zinc chloride, and $\Delta\bar{\nu}$ 396 was attributed to the oscillation of the remaining ion after partial ionization of the molecule. As the degree of ionization is small in ethyl alcohol solutions, this difference between aqueous and ethyl alcohol solutions is understandable. The observed

difference between crystalline zinc chloride (131), which gave $\Delta\bar{\nu}$ 234, and the shift observed from solutions is quite marked and beyond experimental error. These experiments point to complex-compound formations in solution. It might be added that x-ray investigations of alcoholic solutions of alkali halides indicate some type of compound formation (269).

The spectrum obtainable from complex copper compounds has been investigated by Bose and Datta (263). The compounds $[\text{Cu}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ and $[\text{Cu}(\text{NH}_3)_6]\text{Cl}_3$ give a modified line at approximately $\Delta\bar{\nu}$ 568. The compound $[\text{Cu}(\text{NH}_3)_6]\text{Cl}_2$ gave no modified line. The interest was primarily in the vibrations of the complex. The compound $[\text{Cu}(\text{NH}_3)_6]\text{Cl}_3$ was considered a true coordination compound. The spectrum is doubtless incomplete.

Copper, zinc, and cadmium ammonium complexes have been investigated by Joos and Damaschun (265) and Damaschun (233). It is argued that there exists a certain similarity between hydrated salts and ammino compounds. To verify this, comparison was made between aquo compounds and the ammino compounds by the analysis of characteristic oscillations. In none of the salts investigated, however, in aqueous solutions in which the existence of a definite hydrate is assumed, could a Raman line be detected corresponding to the aquo complex. An aqueous solution of copper sulfate gave $\Delta\bar{\nu}$ 434, 600, 979, and $\Delta\bar{\nu}$ 1096. With the corresponding ammino compounds, with two exceptions, an oscillation near $\Delta\bar{\nu}$ 400, characteristic of the complex, was observed. The results are given in table 17.

Ammonium compounds of silver and nickel gave no Raman lines characteristic of the complex. The $\Delta\bar{\nu}$ for the NH_3 group in the complex is appreciably lower than that obtained from pure NH_3 . The frequency displacement for either the complex zinc chloride or complex zinc sulfate becomes less on standing over a period of time, the presumption being the conversion of the hexammino compound to the tetrammino compound under these circumstances.

Freshly made $\text{Zn}(\text{NH}_3)_6\text{Cl}_2$ gives $\Delta\bar{\nu}$ 418. A compound of the composition $(\text{NH}_4)_4(\text{ZnCl}_6)$ gives $\Delta\bar{\nu}$ 274, which was attributed by Damaschun to the anion $(\text{ZnCl}_6)^{\equiv}$. This can be written,

however, as $\text{ZnCl}_2 \cdot 4\text{NH}_4\text{Cl}$, wherein $\Delta\bar{\nu}$ 274 may be attributed to the Raman spectra of zinc chloride. The frequency, however, is slightly less than that observed in zinc chloride solutions ($\Delta\bar{\nu}$ 296). Only the strong inactive frequency of the SO_4 group was recorded in the complex zinc and copper sulfates. These were for $\text{Cu}(\text{NH}_3)_4\text{SO}_4$, $\Delta\bar{\nu}$ 977, and for $\text{Zn}(\text{NH}_3)_6\text{SO}_4$, $\Delta\bar{\nu}$ 979 and 1110. No lines were observed which could be attributed to an inter-chlorine vibration. The absence of frequencies which could be attributed to aquo complexes does not necessarily entirely preclude their existence. They may be too broad to be detected, or,

TABLE 17
Characteristic Raman frequencies of ammino compounds

| COMPOUND | INNER VIBRATION OF COMPLEX | AMMONIA VIBRATIONS |
|---|----------------------------|--------------------|
| | $\Delta\bar{\nu}$ | $\Delta\bar{\nu}$ |
| NH_3 | — | 3223 3306 3394 |
| $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ | 410 | 3309 |
| $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ | 419 | — |
| $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ | — | 3286 3374 |
| $\text{Zn}(\text{NH}_3)_6\text{Cl}_2$ | 418 | 3183 3274 |
| $\text{Zn}(\text{NH}_3)_6\text{SO}_4$ | 428 | 3193 3268 |
| $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$ | 340 | 3287 3372 |
| $\text{Ag}(\text{NH}_3)_2\text{Cl}$ | — | 3305 |

as a result of loose binding, only one excitation stage of oscillation may exist.

Although the cyanides will be discussed briefly under a separate title, two complex cyanides were observed by Damaschun (233) to give shifts ostensibly characteristic of the complex. These are for $\text{K}_3\text{Co}(\text{CN})_6$, $\Delta\bar{\nu}$ 340, for $\text{K}_3\text{Cr}(\text{CN})_6$, $\Delta\bar{\nu}$ 728. However, complex iron, zinc, cadmium, and copper cyanides gave no such displacement. This is also true of $\text{K}_2\text{Hg}(\text{CN})_4$ (229). The compounds $\text{K}_4\text{Ru}(\text{CN})_6$, $\text{K}_3\text{Rh}(\text{CN})_6$, (268) and for $\text{KAg}(\text{CN})_2$, (229) have low frequency shifts.

As has been mentioned, compounds of the type K_2HgCl_4 give a well-defined Raman shift. On the other hand, compounds of the types KCdCl_3 and KAgI_2 give no Raman lines (229). This is pre-

sumably connected with the nature of the homopolar binding. The compound KCdI_3 gives an especially strong line at $\Delta\bar{\nu}$ 118, attributed to the complex. Complex molybdates and tungstates have been investigated by Damaschun (233) with the results indicated in table 18.

For the molybdates, the corresponding largest frequency shifts are sharp and intense. The intermediate shifts are broad and weak. The displacement of $\Delta\bar{\nu}$ 314, which occurs only in Na_2MoO_4 , is broad and strong. Apparently with increasing complexity of the molecular aggregation there is a gradual increase in the magnitude of the larger shifts. Whether or not the aggregations have

TABLE 18
Some Raman frequencies of tungsten and molybdenum complexes

| SUBSTANCE | $\Delta\bar{\nu}$ |
|---|-------------------|
| Na_2MoO_4 | 314 843 896 |
| $\text{Na}_4\text{Mo}_3\text{O}_{11}$ | — 886 937 |
| $\text{Na}_6\text{Mo}_5\text{O}_{21}$ | — 913 959 |
| $\text{Na}_{10}\text{Mo}_{12}\text{O}_{41}$ | — — 953 |
| Na_2WO_4 | 583 930 — |
| $\text{Na}_6\text{W}_5\text{O}_{21}$ | — 961 — |

the formulas assigned to them is another question. The Raman spectra in any case show a measurable alteration.

SUMMARY

The existence of complexes in the gaseous, liquid, and crystalline states of aggregation or in solution, including polymers, more or less definite compounds, and those compounds whose existence is too ephemeral to determine by chemical means, has long been postulated on the basis of the other physical and chemical data. The investigation of these complexes from the point of view of the Raman effect provides a new method of approach which, in time, doubtless will bear considerable fruit. As can be stated of many of the Raman studies, the results are as yet incomplete. Nevertheless, sufficient data have accumulated to aid in the interpretation of the constitution of these substances, particularly in those

cases where other methods are inadequate. Nor does this interpretation rest solely on the Raman spectra of inorganic complexes. From the point of view of organic chemistry it may be demonstrated even more clearly that these interpretations are, in general, correct. Organic polymers, whose constitution is very well known, give Raman spectra perfectly in accord with that constitution, and organic complexes which exist only in solution, likewise, in general, give Raman spectra consistent with the interpretation based upon the behavior of these complexes from an organic point of view.

IX. RAMAN SPECTRA OF AMORPHOUS COMPOUNDS AND MIXTURES

Amorphous materials have been less investigated from the point of view of Raman spectra than any other class of substances. The reason for this lies in the difficulty of eliciting Raman lines from such materials. This is because of the extreme feebleness of the Raman shifts from these compounds. Exposures from days to weeks are often necessary to record the strongest Raman lines. Furthermore, the most common amorphous substance, glass, is so complex that the interpretation of the Raman spectra obtained is very difficult. With improved experimental technique, particularly in the direction of monochromatism, improved optical systems, and greater light intensities, and finally with a systematic investigation of the more simple glasses and simple silicate compounds as a preliminary, it can be predicted that more comprehensive and fundamental information concerning the constitution of amorphous substances will be made available.

It has been shown that Raman shifts from crystals, liquids, gases, and solutions are characteristic of the valence forces, the atomic masses, and the spacial configurations of the molecule. Since amorphous substances also possess these properties, there is no *a priori* reason why they should be an exception. The difficulty probably lies in the imperfect quantization of the vibrational energy, and may be somewhat analogous to the effect of increased pressure, which will be treated later. The lines obtained from amorphous substances are broad and diffuse and can only be

quantitatively investigated by microphotometric means. It may be emphasized, however, that notwithstanding these deterrents, the Raman spectra method offers an almost unique method of investigation for these substances which give no x-ray pattern and which will not yield to the usual physico-chemical methods of approach. The Raman shifts for a number of glasses and amorphous silicon dioxide (fused silica) as compared with crystalline silicon dioxide (quartz) are given in table 19.

The large number of observed frequencies in quartz can only be accounted for by the assumption of a large number of external vibrations, indicating a complicated lattice. So far as fused silica is concerned, it was originally believed that no Raman effect could be observed (149). Later, however, Gross and Romanova (122) obtained a large number of lines agreeing qualitatively with those obtained with the crystalline material. Apparently the intensity relations are not identical, although these estimates are, at best, qualitative.

One of the most intense lines observed in quartz, $\Delta\bar{\nu}$ 125, is missing in all the glasses and in fused silica. This may possibly be due to its close proximity to the exciting line and it may consequently be hidden behind the general background scattering. This point possibly could be clarified by excitation with the 2536 A.U. mercury line and the reabsorption of this line with mercury vapor, at least so far as fused silica is concerned. Any comparison between Raman spectra of the glasses from an intensity point of view is particularly difficult in view of the well-known differences in absorption which small traces of impurity will impart to these substances. On the other hand, the magnitudes of the shifts show more than considerable similarity with that of the other compounds containing silicon dioxide, but at this time the absence of particular frequencies cannot be given great weight. It may be stated, however, that those glasses which have a high index of refraction show relatively greater intensities in the bands near $\Delta\bar{\nu}$ 1000 and $\Delta\bar{\nu}$ 1080 than the earlier members of the series. The same may also be said of the band lying between $\Delta\bar{\nu}$ 460 and 500. However, the relative intensity between these two groups ($\Delta\bar{\nu}$ 460-520 and $\Delta\bar{\nu}$ 1080 (max.)) suffers a reversal in passing

TABLE 19
Raman spectra of amorphous compounds

| COMPOSITION | REFRACTIVE INDICES | RAMAN SHIFTS* | | | | | | | | | | | | | | | REFERENCES | | | | |
|------------------------------|--------------------|------------------|------------------|------------------|-------|----------------------|----------------------|------------------|-------------------|-------------------|----------------------|-------------------|------------------|-------|------------------|--------|------------|-------------------|------|--------|-------|
| Crystalline quartz | | 125 _s | 207 _m | 264 _w | (320) | 358 | 405 | 463 _m | 503 | 526 | 585 | 633 | 694 _w | (746) | 800 _w | 943 | 1020 | 1075 _w | 1163 | (1220) | (122) |
| Amorphous silica | | 213 | 263 | 323 | 370 | 440 _s | 500 | 625 _w | 670 | 740 | 800-830 _m | 1030-1090 | 1190-1240 | | | | | | | | |
| Crown glass | | 208 | 270 | 330 | 385 | 450-510 | 460 | 625 | 670 | 740 | 800-830 | 1030-1090 | 1140-1190 | | | | | | | | |
| Fluor crown | 1.4933 | | | | | 460 | 460 | | | | 780 | 1080 | | | | | | | | | (272) |
| U. V. crown | 1.5035 | | | | | 460 | 460 | | | | 780 | 1080 | | | | | | | | | |
| Prism crown | 1.5163 | | | | | 460 | 460 | | | | 780 | 1080 | | | | | | | | | |
| Silicate crown | 1.5191 | | | | | 460-520 _m | 510 | 590 | 670 | 740 | 800 | 970 | 1140 | 1190 | 1320 | | | | | | |
| Flint glass | 1.5286 | 208 | 260 | 323 | 370 | 450 | 460-520 _s | 590 | 670 | 740 | 800 | 970 | 1140 | 1190 | 1320 | | | | | | (122) |
| Telescopic flint | 1.5286 | | | | | 460-520 _s | 460 | 640 _w | 800 | 800 | 800 | 1065 _m | 1330 | | | | | | | | |
| Baryta light flint | 1.5694 | | | | | 460 | 460 | | | | 780 | 1080 | | | | | | | | | |
| Densest borosilicate crown | 1.5726 | | 340 | | | 460 | 460 | 650 _w | 800 | 800 | 800 | 1090 _m | 1320 | | | | | | | | (272) |
| Ordinary light flint | 1.5774 | | | | | 460-500 | 460-500 | 780 _w | 1000 _s | 1080 _s | 1000 _s | 1080 _s | 1320 | | | | | | | | |
| Baryta light flint | 1.6042 | | | | | 460-500 _m | 460-500 _m | | 1000 _s | 1080 _s | 1000 _s | 1080 _s | 1320 | | | | | | | | |
| Ordinary flint | 1.6202 | | | | | 460-520 _m | 460-520 _m | | 1000 _s | 1080 _s | 1000 _s | 1080 _s | 1320 | | | | | | | | |
| Plate glass | | 268 | | | | | | | | | 785 | 1070 | 1293 | 1657 | 1860 | (2309) | | | | | (126) |
| 75 per cent SiO ₂ | | | | | | | | | | | | | | | | | | | | | |
| Plate glass | | 259 | | | | 471 | 537 | 647 | 785 | 1071 _s | 1748 | | | | | | | | | | (127) |
| Pyrex glass | | | 400 | | | | | | | | 780 | | | | | | | | | | (180) |

* See footnote to table 8.

from the lower index glasses to the higher index glasses, although the absolute intensity of both groups is less in the lower index members. The increasing intensity of the Raman shifts with increasing index of refraction may possibly be attributable to the closer approach of the exciting radiation to the characteristic ultra-violet absorption in these glasses, that is, when the absorption frequency approaches the value $\frac{E_n - E_k}{h}$ where E_n is the energy of the "third level," discussed in the section on "Theory" (p. 351). Since the ultra-violet absorption is determined largely by the impurities present, this explanation may not be tenable. In some of the glasses larger frequency shifts between $\Delta\bar{\nu}$ 1293 and $\Delta\bar{\nu}$ 1748 appear which are not present in either amorphous or crystalline silica. These cannot be attributed to external vibrations. It is also extremely unlikely that these shifts would appear in the glasses and not in crystalline silica if their presence were possible in both materials. The shift $\Delta\bar{\nu}$ 2309, noted by Hol-laender and Williams (126) is probably erroneous. $\Delta\bar{\nu}$ 1320, observed by Bhagavantam (272) appears in some of the glasses studied by him but not all. The absence is without significance.

It has already been mentioned that Weiler (159, 160) considers $\Delta\bar{\nu}_1$ 1170–1208, $\Delta\bar{\nu}_2$ 1062–1086, $\Delta\bar{\nu}_3$ 800, and $\Delta\bar{\nu}_4$ 502 as the fundamental vibrations of the SiO_4 group (276).

It has been shown by Bragg and Gibbs (273) and Wyckoff (278) that in quartz, for example, each silicate atom is surrounded by four oxygen atoms, giving nearly a tetrahedral structure, the group unit being, therefore, from the point of view of Raman spectra, SiO_4 rather than SiO_2 . The problem, therefore, is really in relating the Raman spectra of amorphous silicates to other compounds containing an SiO_4 group, whose degree of polymerization can be more easily ascertained and whose composition can be more readily investigated by other physico-chemical processes.

The frequency shifts given above as characteristic of the SiO_4 group have been obtained from a systematic study of a series of esters of silicic acid. This investigation by Weiler (160) yielded the results given in table 20.

The structure and constitution of the esters has been investi-

gated by Staudinger (277), Eulitz (274), and Konrad, Bächle, and Signer (275). The four frequencies given in the table were considered characteristic of the inner vibrations of the SiO_4 group. The changes in the frequency shifts were attributed to the influence of polymerization. In addition to a large change in magnitude, $\Delta\bar{\nu}_4$ also decreases markedly in intensity with increase in polymerization. The latter two shifts, $\Delta\bar{\nu}_3$ and $\Delta\bar{\nu}_4$, were considered inactive and due to symmetrical oscillations. The first two frequencies, $\Delta\bar{\nu}_1$ and $\Delta\bar{\nu}_2$, are more or less independent of the decrease of polymerization. It is concluded that the Raman spectra of the silica esters approach more and more closely that of quartz as the polymerization increases, and that this is def-

TABLE 20
The group frequencies of SiO_4 in silicic acid esters

| COMPOUNDS | $\Delta\bar{\nu}_1$ | $\Delta\bar{\nu}_2$ | $\Delta\bar{\nu}_3$ | $\Delta\bar{\nu}_4^*$ |
|---|---------------------|---------------------|---------------------|-----------------------|
| Monomeric ester, $\text{SiO}_4 \cdot (\text{CH}_3)_4$ | 1205 | | | |
| | 1192 | 1110 _w | 842 _m | 642 _s |
| | 1170 | 1080 _w | | |
| Dimeric ester, $\text{Si}_2\text{O}_7 \cdot (\text{CH}_3)_6$ | 1195 | 1092 _w | 827 _m | 576 _m |
| Trimeric ester, $\text{Si}_3\text{O}_{10} \cdot (\text{CH}_3)_8$ | 1190 | 1090 _w | 825 _m | 556 _w |
| Decameric ester, $\text{Si}_{10}\text{O}_{30} \cdot (\text{CH}_3)_{22}$ | 1194 | 1086 _w | 825 _m | 518 |

* See footnote to table 8.

inite evidence, therefore, of the polymerized character of the SiO_4 group as regards the crystalline and amorphous silicates. If the four fundamental frequencies attributed to the SiO_4 group are, in fact, such, then there remains a large number of lines which are present in quartz to be accounted for. This has been essayed on the basis of combination frequencies not only for those observed in Raman spectra but also in infra-red absorption spectra. There is a reasonably good agreement between twenty-seven lines observed and calculated on this basis. There are, however, some disagreements both in regard to the expected intensities and to some of the shifts actually observed in quartz.

Further experiments in this direction will undoubtedly clarify these anomalies. In any case, the results are of considerable interest.

Other than silicate glasses, few amorphous compounds have been investigated in the inorganic field. A glass made from potassium alum, the product being transparent, hard, brittle, and exhibiting no x-ray pattern, was briefly examined by Hibben (125). The normal Raman shifts found in concentrated solutions of potassium alum, with the exception of $\Delta\bar{\nu}$ 982, were considerably broadened and more diffuse. The latter shift remained fairly sharp and strong. Silicate glasses of widely varying compositions have not been examined. It is not surprising that those glasses which contain silicon dioxide as a large portion of their composition should exhibit frequencies which can be more or less ascribed to the silica group.

The glasses of high index, however, contain PbO in quantities almost equal to the silica content. This would presumably result in oscillations corresponding to very small $\Delta\bar{\nu}$ not observed as yet.

SUMMARY

The Raman spectra investigation of amorphous substances is yet in its infancy. Notwithstanding certain inherent difficulties, considerable progress has been made. To interpret and evaluate the results obtained from these particular investigations requires as a preliminary a thorough and systematic study of the Raman spectra from the other states of aggregation. This has now reached a point of exactness where these results may be applied to amorphous compounds with confidence, when additional experimental data are available.

X. THE RAMAN SPECTRA OF PURE LIQUIDS

The Raman spectra of pure liquids offer the advantage of high concentration; that is to say, the material to be examined consists of a single component, and any results obtained may be attributed to that component alone without the influence of ionization in solution and without the general scattering which is usually concomitant with the Raman spectra of crystals. This is particularly true of organic substances, which usually readily lend themselves to examination under these conditions. Inorganic

materials, which may be examined in liquid form, are relatively rare. It may be stated, however, in general, that apart from the influence of the electrical environment, which is present in solution, the Raman spectra of liquids are consistent with the Raman spectra of the substances in the gaseous or solid state of aggregation. In some cases it is necessary to operate at a temperature of sufficient elevation that the number of molecules in the first vibrational level is not entirely negligible. This is also particularly true of the gases, as will be seen later. The zero vibrational level of the gases is usually at room temperature or considerably below. In the case of liquids, room temperature does not as a rule excite molecules above the zero vibrational level. One has in this case the advantage of increased concentration without lattice vibrations and without ionization effects. On the other hand, some of the compounds are not without color, which means that in order to register the Raman lines the exciting radiation must be of sufficiently long wave length that the Raman radiation which is emitted will not be absorbed by the medium, a process which would result otherwise in relatively increased exposure.

The results are, as a rule, confined to the halogens since these exist most readily in liquid state. Carbon tetrachloride is omitted from consideration since it perhaps more properly belongs to the category of organic compounds. At the same time, however, carbon disulfide is considered as belonging to inorganic compounds, the distinction being somewhat arbitrary. In general, as is to be expected, the principal frequencies to be obtained are four in number, from molecules of the type AX_3 , the fourth fundamental frequency, according to Bhagavantam (111), coming out with relatively greater intensity than the others. Furthermore, the oscillation frequency becomes smaller with increasing atomic weight. It is interesting to note that with increasing atomic weight the interval between the third and fourth Raman frequencies continues to increase, whereas that between the first and second decreases. In the case of the compounds of the type AX_4 , all the substances show four principal Raman frequencies, the third being the most prominent in every case. The results are given in table 21.

TABLE 21
Raman spectra of inorganic liquids

| COMPOUND | RAMAN SHIFTS* | | | | REFERENCES |
|---------------------------------------|-----------------------------------|---|---|---|--|
| AsCl ₃ | 158 _m 194 _w | 370 _w | 405 _s | | (235, 24, 23, 111, 227, 21, 22, 230) |
| AsBr ₃ | 6 _m 120 _m | 273 _s | 320 _m 360 _s | | (230) |
| SbCl ₃ | 130 _s 155 _m | | | | (235, 287, 23, 24, 230) |
| BCl ₃ | | 255 _m | 472 _m | 947 _w | (306) |
| PCl ₃ | 100 _s | 258 _s (340) | 484 _m 511 _s (580) | (1340) | (235, 24, 111, 227, 209, 270, 286, 23, 284, 21, 306, 22, 230) |
| PBr ₃ | 116 _s 162 _m | 380 _s | 400 _s | | (235, 24, 270, 285, 22) |
| POCl ₂ | 192 _m | 268 _w 338 _m | 485 _s | (1290) | (291, 209, 306, 22) |
| SiCl ₄ | 151 _m 221 _m | 425 _s | 485 _s (583) | 607 _w | (149, 235, 111, 227, 300, 24, 15, 16, 304, 270, 22) |
| SiBr ₄ | 90 _m | 137 _m | 249 _s | 487 _w | (270) |
| SiHCl ₃ | | 179 _m | 250 _m | 489 _s | (305, 282, 200) |
| SnCl ₄ | 104 _m 132 _m | 366 _s | 404 _m | 587 _m 799 _m | (235, 24, 298, 111, 304, 227, 22, 291, 15, 16) |
| SnBr ₄ | 66 _w 88 _m | (159) 220 _s 279 _m | 386 _s | 497 _m | (304) |
| TiCl ₄ | 120 _m 144 _w | 386 _s | 412 | 647 655 _s 798 _w (848) | (235, 111, 227, 304, 24, 15, 16) |
| CS ₂ | | | | (1220) | (299, 296, 297, 288, 166, 155, 111, 227, 279, 131, 292, 295, 289, 280, 281, 307, 15, 98) |
| SO ₂ Cl ₂ | | 213 _m 278 _w | (365) 387 _m 409 _s | 559 _m (576) | 1187 _m |
| S ₂ Cl ₂ | 109 _s | 206 _w 247 | 447 _s (545) | | (291, 292, 209, 22, 293) |
| SOCl ₂ | 193 _s | 282 _m 343 _s | 444 _w 488 _m | 1229 _s | (292, 209, 293, 306) |
| HgCl ₂ | | 314 _m 376 | | | (292, 209, 306, 22, 293) |
| HgBr ₂ | | 195 | | | (230) |

* See footnote to table 8.

Comparing phosphorus trichloride with phosphorus oxychloride, essentially the same lines exist in both cases with the exception of $\Delta\bar{\nu}$ 511, which is absent in phosphorus oxychloride and very intense in phosphorus trichloride. Furthermore, the intensity of $\Delta\bar{\nu}$ 338 is relatively strong in phosphorus oxychloride and is just detectable in phosphorus trichloride. This may possibly be attributed in phosphorus oxychloride to phosphorus trichloride as an impurity. The line appearing at approximately $\Delta\bar{\nu}$ 1290 is attributed by Venkateswaran (306) and Nisi (209) to the P=O group. Boron trichloride gives only three detectable frequencies, although $\Delta\bar{\nu}$ 947 shows some doublet structure. Marked changes in the intensities of the Raman lines are noticed as compared with the other chlorides, the second frequency coming out more prominently.

The change in the Raman spectra of mixtures of phosphorus trichloride and phosphorus tribromide and of stannic chloride and phosphorus tribromide as a function of the relative proportion of the constituents indicating close compound formation has been mentioned in the Raman spectra of inorganic compounds (270, 271). In the compound SiHCl_3 , $\Delta\bar{\nu}$ 2258 corresponds to an $\text{H}\leftrightarrow\text{Si}$ vibration, which is appreciably less than the shift corresponding to the $\text{C}\leftrightarrow\text{H}$ or $\text{S}\leftrightarrow\text{H}$ vibrations and would indicate a slightly less binding force existing between the silica atom and the hydrogen atom than that between the carbon and hydrogen atoms and between the sulfur and hydrogen atoms.

The principal frequencies observed for carbon disulfide are $\Delta\bar{\nu}$ 655 and 800. The number of frequencies and their characters are connected with the fact that carbon disulfide is a linear model of the type AX_2 , and is included in this discussion in order to elucidate the structure of other inorganic compounds containing sulfur. The $\text{C}\leftrightarrow\text{S}$ vibration is possibly established from a study of organic compounds containing sulfur, which will be discussed in more detail in a subsequent publication. It suffices to say, that $\Delta\bar{\nu}$ 650 to 704 and $\Delta\bar{\nu}$ 740 to 805 are prominently present in mercaptans and organic sulfides (260). These lines, however, split into several components, depending upon the complexity of the structure of the remainder of the molecule. The characteristic

frequency of the $S \leftrightarrow S$ vibration, as is apparent in the organic disulfides, becomes $\Delta\bar{\nu}$ 512 and is entirely absent in the monosulfides. The relatively low frequency obtained for this vibration would apparently indicate a single bond binding in the case of the disulfides. On this assumption the frequency to be expected for $S=S$ would occur at $\Delta\bar{\nu}$ 724, these two frequencies bearing the ratio of one to the other as the $\sqrt{2}$. The frequency $\Delta\bar{\nu}$ 724 is approximately that obtained from the absorption spectra of sulfur vapor. The Raman spectra of sulfur crystals and sulfur dissolved in carbon disulfide do not show this frequency, which is reasonably explicable on the grounds that under these conditions the sulfur is not present in the form of S_2 , but is present in the form of a higher polymer. From the same point of view, however, it must be noted that one of the few apparent inconsistencies in this line of reasoning lies in the structure of carbon disulfide, since the frequencies characteristic of this compound, which is generally considered as $S=C=S$, do not vary greatly from those obtained from the mercaptans where the characteristic frequency is attributed to the $C-S$. It is quite evident, however, that the constitution of carbon disulfide is symmetrically arranged in regard to the sulfur atoms. On the other hand, it is not wholly impossible that the ordinary conception of the constitution of carbon disulfide may be in error. Nisi (209) has attributed $\Delta\bar{\nu}$ 1200 (approximate) to an $S \leftrightarrow O$ oscillation, the frequency appearing in $SOCl_2$ and SO_2Cl_2 but being absent in S_2Cl_2 . Thionyl chloride is consistent with this view. According to Venkateswaran (306), Cabannes and Rousset (22), and Matossi and Aderhold (292), the structure of this compound is $Cl_2S=O$. The molecule is considered by Cabannes and Rousset to have a pyramidal configuration and give rise to the six observed Raman frequencies. One of the frequencies observed occurs when the sulfur atom remains fixed and the chlorine and oxygen atoms vibrate symmetrically. Another occurs when the two chlorine atoms remain fixed and the oxygen and sulfur oscillate against each other. The third occurs when the SO group oscillates as a unit against the two chlorine atoms, which in turn vibrate along the line of the binding force against the SO group. $\Delta\bar{\nu}$ 488 represents the first of these types

of oscillations, $\Delta\bar{\nu}$ 1229 the second, and $\Delta\bar{\nu}$ 193 the third. The other frequencies represent displacements transverse to the chemical bond.

The compound sulfur monochloride has the formula S_2Cl_2 . This may be written in two ways, $S=SCl_2$ or $Cl-S-S-Cl$. According to Michaelis and Schifferdecker (294) and Thorpe (302, 303), the former structure is correct, analogous to thionyl chloride. On the other hand, Bruni and Amodori (283) favor the latter structure. The latter is consistent with the view of Sugden (301). The principal shifts of this compound are $\Delta\bar{\nu}$ 109, 206, 247, 447. The existence of these frequencies demonstrates that the compound cannot be, in liquid form, diatomic, that is, SCl . Venkateswaran (306) argues that the absence of a higher frequency shift above $\Delta\bar{\nu}$ 1100 and a lower frequency shift at 280 is evidence against a similarity in structure between S_2Cl_2 and $COCl_2$. More important, however, is the presence of a frequency shift near $\Delta\bar{\nu}$ 512, corresponding to $S-S$ and the absence of a frequency near $\Delta\bar{\nu}$ 724, attributed to $S=S$. This is in contrast to the view of Matossi and Aderhold (292), who consider that $\Delta\bar{\nu}$ 451 is attributable to the $S=S$ vibration and in consequence the structure is similar to thionyl chloride. This view was also held by Meyer (293). The difference in views rests in the assignment of Raman frequencies to characteristic vibrations. A determination of the Raman spectrum of sulfur vapor will possibly help clarify the matter.

SUMMARY

While the field of Raman spectra investigation in inorganic liquids is relatively small as compared with that of solutions or crystals, it has been by no means extensively studied. There is no *a priori* objection, except as a matter of experimental inconvenience, to the study of many other such compounds as those given, when in a molten state. The limiting factor is primarily a maximum temperature of approximately $450^\circ C.$, wherein the black-body radiation becomes appreciable in long exposures. In general, the results are consistent with those from compounds with the constitution and configuration assigned to them. In the specific

cases, ostensible disagreements with the precepts heretofore set forth are not disagreements with those precepts as such, but rather questions of interpretation. In all such cases further investigation will doubtless clarify disputed points

XI. THE RAMAN SPECTRA OF CYANOGEN COMPOUNDS

The Raman spectra of cyanides offer an interesting application of Raman spectra methods. The results, while enlightening, are not wholly satisfactory with particular regard to the sulfo-cyanates. The Raman frequencies are given in tabular form in table 22.

The first striking observation is the fact that the wave-number shift for the cyanogen group falls within the region which can be attributed to a triple bond rather than a double bond. Hence it may be stated that the $C \leftrightarrow N$ oscillation, at least from the Raman spectra point of view, involves a triple bond. The classical method of considering the isocyanates, that is, compounds of the constitution $R-N=C=O$, and the isothiocyanates, $R-N=C=S$, is in the manner just given and that of the isocyanides, as $R-N=C$, while the nitriles or cyanides are considered $R-C \equiv N$. It is evident that this is not consistent with the Raman spectra data.

The wave-number shift near $\Delta\bar{\nu}$ 2100 is quite characteristic of all compounds containing the CN group with the possible exception of dicyanine, in which compound it is raised to a somewhat higher frequency. In hydrogen cyanide gas, this shift is $\Delta\bar{\nu}$ 2089. In hydrogen cyanide liquid, according to Bhagavantam (279), this has degenerated to a triplet. In organic compounds the shift is somewhat higher, methyl cyanide, for example, giving a shift of $\Delta\bar{\nu}$ 2246. The isothiocyanides and isocyanides are confined to organic compounds, and will not be discussed in detail here. The shifts, however, are of the same order of magnitude, but in the former compounds are generally much broader. In the cyanates the formerly accepted constitution would include a double bond for oxygen. From the Raman spectra obtained, this does not seem possible.

In spite of the complexity of the ions in some of the compounds

TABLE 22
Raman spectra of cyanogen compounds

| COMPOUNDS | RAMAN SHIFTS* | REFERENCES |
|---|-------------------------------------|--|
| HCN, gas, at 80°C..... | 2089 _m | (315) |
| HCN, liquid..... | 2069 2096 _s (2122) | (312, 309, 310, 279, 315, 308, 311) |
| NaCN, crystalline..... | 2085 _m | (96) |
| KCN, solution..... | 2081 | (316, 309, 310, 298, 318, 261, 229, 225, 263, 199) |
| (CN) ₂ , liquid..... | 512 (756) 860 | (318) |
| Hg(CN) ₂ , solution..... | 260 _w | (318, 261, 229, 225) |
| Hg(CN) ₂ , crystalline..... | 276 | (96) |
| KAg(CN) ₂ , solution..... | 239 _w | (96, 316, 318, 229) |
| KCu(CN) ₂ , solution..... | 855 | (317) |
| K ₂ Cu(CN) ₄ , solution..... | 2130 _w | (229, 233) |
| K ₂ Cd(CN) ₄ , solution..... | 2110 | (229, 233, 317) |
| K ₂ Fe(CN) ₅ ·3H ₂ O, crystalline..... | 2142 | (96) |
| K ₂ Fe(CN) ₆ , solution..... | 2051 _m 2092 _m | (233) |
| K ₂ Ni(CN) ₄ , solution..... | 2144 _m | (268) |
| K ₂ Ni(CN) ₄ (?) ₂ , solution..... | 2142 _m | (268) |
| K ₂ Hg(CN) ₄ , solution..... | (2055) | (229, 317) |
| K ₂ Zn(CN) ₄ , solution..... | 2130 | (317, 233) |
| K ₂ Cr(CN) ₆ , solution..... | 782 | (233) |
| K ₂ Cr(CN) ₅ , solution..... | 619 | (268) |
| K ₂ Cr(CN) ₄ , solution..... | 340 _m (405) | (268) |
| K ₂ Ru(CN) ₆ , solution..... | 381 | (268) |
| K ₂ Rh(CN) ₆ , solution..... | 593 | (268) |
| NaSCN, solution..... | 754 _w | (313, 314, 319) |
| KSCN, solution..... | 747 _m | (313, 314, 316, 318, 96) |
| KSCN, crystalline..... | 747 _m | (96) |
| NH ₄ SCN, solution..... | 744 _m | (96) |
| NH ₄ SCN, crystalline..... | 776 | (313, 314, 316, 96) |
| Ba(SCN) ₂ , crystalline..... | 838 _w 1229 1314 | (96) |
| KOCN..... | 397 _w | (316) |
| ClCN..... | 368 _w | (323) |
| BrCN..... | 580 _m | (323) |
| ICN..... | 321 470 _m | (323) |
| | 2158 _s | |

* See footnote to table 8.

given, relatively few Raman shifts are observable. $\Delta\bar{\nu}$ 782 for $K_3Cr(CN)_6$ and $\Delta\bar{\nu}$ 340 for $K_3Co(CN)_6$ have been attributed to the oscillation of the complex (233). The same might be said of $\Delta\bar{\nu}$ 855, observed in $KAg(CN)_2$. The shift $\Delta\bar{\nu}$ 838 possibly observed in potassium cyanide solution (316) is doubtful. Otherwise, the shifts appearing near $\Delta\bar{\nu}$ 750 appear exclusively in those compounds containing sulfur, and are attributed to the triatomic nature of the ion. This may also be said of the shift $\Delta\bar{\nu}$ 838 observed in potassium cyanate (316). Otherwise, there is present a somewhat curious anomaly, namely, the compounds containing heavy cations have larger frequency shifts than those compounds which contain lighter ones. This is diametrically opposed to observations with other compounds, and has been explained by Pal and Sen Gupta (317) as due to a change in the binding force which is influenced by the electronic configuration surrounding the atom. Krishnamurti (96) attributes $\Delta\bar{\nu}$ 260 and 276 in mercuric cyanide (solution or crystalline) to the $Hg \leftrightarrow CN$ oscillation, and considers the molecule as linear, the binding force being mainly homopolar. The larger frequency shift ($\Delta\bar{\nu}$ 2100) is greater with an increase in the homopolar nature of the R—CN binding. The same view is taken by Samuel and Kahn (268). In the thiocyanates the decrease in the CN shift is attributed by Krishnamurti to the influence of a double bond between the sulfur and the carbon atom, the carbon being supposed to be joined to the nitrogen by a double bond in the classical manner. $\Delta\bar{\nu}$ 747 is considered characteristic of S=C. This view does not seem to be particularly tenable, first because the magnitude of the frequency shift corresponding to the $C \leftrightarrow N$ oscillation is greater than that to be expected from a double bond linkage; second, this shift is not radically different from that ascribed by Krishnamurti to the triply bonded CN linkage in other compounds; and last, $\Delta\bar{\nu}$ 747, ascribed to an S=C oscillation, is quite close to the C—S oscillation observed in mercaptans and methyl sulfides. The latter difficulty has been mentioned in discussing the shifts observed in carbon disulfide. If the assumption as to the nature of the triple bond between carbon and nitrogen is correct, which seems probable, then the constitution of the thiocarbimides can only involve a single bond between

the carbon and sulfur. There are two lines which fall within this region, namely $\Delta\bar{\nu}$ 645 (s) and $\Delta\bar{\nu}$ 796 (w) in ethyl thiocarbimide (309, 310).

Dadieu and Kohlrausch (193) presume a ring structure between the nitrogen, carbon, and sulfur atoms which would account both for the triple bond between the carbon and nitrogen and for the single bond between the carbon and sulfur in these compounds. The triple bond in the cyanogen group and isonitrile is also assumed by Sugden (322). He does, however, assume a double bond between the carbon and sulfur in the thiocarbimides on the basis of the parachor. In this case, however, he is not able to distinguish between the constitution $\text{N}\equiv\text{C}-\text{S}$ and $\text{N}=\text{C}=\text{S}$, the two giving identical results (321). The difficulty is that the C—S oscillation varies over some seventy wave numbers, coupled with the fact that the generally accepted constitution of carbon disulfide falls within approximately the same range. While the latter is supposed to have no electric moment and consequently is presumably linear (320), a ring structure in this compound would make compatible all of these data. It remains to be seen what further investigations will provide to clarify this point.

There is no apparent reason why the shifts observed for a solution of potassium ferrocyanide should be appreciably less than that observed in the crystal—or at least it is not clear why there is a difference of the magnitude indicated.

The constitution of the cyanides and the isonitriles is fairly conclusively demonstrated by these Raman spectra investigations. This differs from the constitution formerly assumed for these compounds. The constitution of the isothiocyanates or thiocarbimides is not quite as clearly defined. The isocyanates, on the other hand, would indicate the absence of a double bonded oxygen and the presence of a triple bond between the carbon and nitrogen. The triple bond structure of the cyanides is likewise supported by the work of West and Farnsworth (323), who have investigated the cyanogen halides both in liquid state and in alcoholic solution. For each halogen derivative three frequency shifts were observed, each, in descending order, depending upon the mass of the substituent halogen. The molecule is considered

linear, and it is concluded that the magnitude of the carbon-nitrogen linkage remains relatively constant, while the valence force joining the halogen to the carbon steadily decreases in the order of chlorine, bromine and iodine.

XII. THE RAMAN SPECTRA OF GASES

The Raman spectra of gases have been reserved for final consideration, first because gases have been partially discussed in the section on "Theory," and second because their spectra are of perhaps more interest to the physicist than to the chemist. Inseparable from this discussion are the Raman spectra of gases in the solid states of aggregation and in solution, where the solubility of the gas is sufficient to make the latter investigation possible.

There are essentially three types of Raman lines occurring in gases: first, those which are purely rotational Raman spectra and which may also occur in the liquid state; second, vibrational Raman spectra, which are of the type which has been dealt with almost exclusively up to this point; and, third, rotational-vibrational Raman spectra, which occur when the vibrational quantum number changes and superimposed on this is also a change in the rotational quantum number. In table 23 are given the *vibrational* Raman spectra of the gases, liquids, and solids for those compounds which generally occur in a gaseous state.

In the case of hydrogen and carbon disulfide there are included in the table some of the vibrational-rotational Raman spectra. Diatomic molecules, such as hydrogen, oxygen, and nitrogen have only one Raman line corresponding to a transition from the zero to the first vibrational level. In the case of oxygen and nitrogen in a liquid state, however, two lines appear which doubtless have been clearly explained by Rasetti (359) as due to the absorption of two quanta of incident radiation, the shifts $\Delta\bar{\nu}$ 3085 and $\Delta\bar{\nu}$ 4633 being almost exact multiples of the primary quantum transition, corresponding to $\Delta\bar{\nu}$ 1552 and $\Delta\bar{\nu}$ 2330. Rotational transitions have been observed for hydrogen, nitrogen, carbon dioxide, ammonia, and hydrogen chloride. Other gases show evidence of rotational effects sometimes characterized as "wings," which are imposed upon the vibrational shifts, but which cannot as a rule be re-

TABLE 23
Raman spectra of compounds generally occurring in a gaseous state

| COMPOUNDS | RAMAN SHIFTS* | REFERENCES |
|--|---|---|
| H ₂ , gas..... | 4125 4143 _w 4158 _a 4162 4714 | (362, 366, 165, 332, 330, 83, 333, 336, 58) |
| H ₂ , liquid..... | 4158 _a | (351, 350, 352, 97, 354, 349) |
| O ₂ , gas..... | 1556 _a | (362, 366, 329, 331, 83, 369, 58) |
| O ₂ , liquid..... | 1552 _a 3085 | (350, 352, 351, 349) |
| O ₂ , gas..... | 1280 _w | (370) |
| N ₂ , gas..... | 2331 _a | (362, 366, 329, 331, 83, 58) |
| N ₂ , liquid..... | 2330 _b 4633 | (363, 352, 351, 349) |
| CO ₂ , gas..... | 1241 1265 _w 1286 _m 1305 1325 1344 1369 1380 _a 1409 _w 1433 | (341, 329, 361, 83, 344, 345, 347, 353, 58) |
| CO ₂ , liquid..... | 1283 _m | (355, 353) |
| CO ₂ , solid..... | 1285 _m | (353) |
| CO, gas..... | 2146 _w | (361, 363, 364, 334) |
| COS..... | 524 (678) 859 _a 1041 1383 2055 | (232) |
| NH ₃ , gas..... | (934) (964) | (341, 104, 372, 324, 325) |
| NH ₃ , solution..... | 1073 (1615) | (116, 343, 365, 233, 371, 346) |
| NH ₃ , liquid (room temperature)..... | 1070 1594 | (341, 111, 226, 227, 232, 340, 298) |
| NH ₃ , liquid (low temperature)..... | 1070 1580 | (287, 24) |
| N ₂ O, gas..... | 1170 (1185) 1260 1284 _b | (341, 329, 347, 83, 327, 348) |
| N ₂ O, liquid..... | 1231 _a | (355, 341) |
| (NO ₂) ₂ at -80°C..... | 275 _m | (356) |
| NO..... | 1877 | (362, 366, 334, 101) |
| H ₂ O, vapor..... | (984) 1648 3654 | (62, 169, 180) |
| H ₂ S, gas..... | 2615 _m | (328, 83) |
| H ₂ S, liquid..... | 2578 _m | (328, 232) |

| | | | | | |
|---|--|------------------|------------------|-------------------|--------------------------------|
| SO ₂ , gas..... | 1154 _s | | | | (279, 83) |
| SO ₂ , solution..... | 1136 _s | | | | (202) |
| SO ₂ , liquid..... | 526 1145 _s 1334 _m 1340 | | | | (197, 111, 227, 309, 232, 292) |
| SO ₃ , liquid..... | 290 _m 370 _s | 535 _m | 686 _w | 1085 _s | (226, 227, 12) |
| S ₂ O ₃ , liquid..... | | | 697 _w | 1271 _s | (226) |
| HCl, gas..... | | | | 1403 _m | |
| HCl, liquid..... | | | | 2778 _m | (373, 374, 372, 222) |
| HCl, solid..... | | | 2780 | 2880 _m | (366, 340, 210) |
| HBr, gas..... | | | | | (365a) |
| HBr, liquid..... | | | | | (367, 368) |
| HBr, solid..... | 2465 | 2487 | | | (367, 368) |
| HI, gas..... | 2235 _w | | | | (365a) |
| Cl ₂ , liquid..... | 556 _s | | | | (367, 368) |
| | | | | | (111, 337, 339) |

* See footnote to table 8.

solved into definite lines. On account of the low concentration of scattering material, the determination of the Raman spectra of gases is difficult. This has been partially solved by increasing the pressure, but as will be seen later, apart from physical imitations, the rotational transitions will not appear when the pressure exceeds certain critical limits.

In table 24 are given the Raman spectra of hydrogen liquid as determined by McLennan, Smith, and Wilhelm (97), and the transitions observed in hydrogen gas by Rasetti (360). The strongest line is that which corresponds to the transition from the zero vibrational to the first vibrational level, $\Delta\bar{\nu}$ 4156. The shifts $\Delta\bar{\nu}$ 354, 587, 814, and 1034 are rotational transitions occurring in the zero vibrational level and correspond to a change in the rotational quantum number in units of two, two of the lines occurring as anti-Stokes lines. The shifts occurring above $\Delta\bar{\nu}$ 4156 are changes in the rotational quantum number concomitant with a shift in the vibrational quantum number 0 to 1, as indicated.

In the liquid the resolution was not sufficient to determine whether the transition corresponding to $\Delta\bar{\nu}$ 4156 corresponded to the 0→0 or 1→1 rotational level.

McLennan, Smith, and Wilhelm (97) have been able to follow the conversion of ortho- to para-hydrogen by means of changes in intensity of the rotational Raman spectra as a function of time. The 0→2 transition doubles in intensity in two days' time, while the 1→3 transition decreases in intensity relative to 0→2. In other words, $\Delta\bar{\nu}$ 587 decreases and $\Delta\bar{\nu}$ 354 increases in their relative intensities in liquid hydrogen during the first forty-eight hours after preparation.

While some rotational spectra have been noted for oxygen by Rasetti (58), nitrogen gives much better results. The results seem to support the hypothesis that in a normal state only even rotational levels are present, or at least that they have a higher statistical weight than the odd ones. The spacing of the lines corresponding to $\Delta\bar{\nu}$ 16 and the transitions observed occur between $\Delta j = 6$ to $\Delta j = 16$ in steps of $\Delta j = \pm 2$.

Rotational transitions in the zero vibrational level for carbon dioxide have been observed by Houston and Lewis (345). The

$\Delta\bar{\nu}$ observed occur between 11.6 and 55.5, advancing in increments corresponding to $\Delta\bar{\nu}$ 3, a total of fifteen lines being registered. These correspond to changes in the rotational quantum number, beginning with $\Delta j = \pm 2$. From these values the moment of inertia, $I = 70.2 \times 10^{-40}$ g. cm.² is calculable. It was originally supposed that some of the vibrational Raman spectra represented combination scattering (361), but more recently $\Delta\bar{\nu}$ 1289 is presumed to owe its origin to the inactive frequency, $\Delta\bar{\nu}$

TABLE 24

| MOLECULAR TRANSITIONS OBSERVED IN H ₂ GAS | | | MOLECULAR TRANSITIONS OBSERVED IN H ₂ LIQUID | | |
|---|------------|-------------------|--|------------|-------------------|
| <i>n</i> | Δj | $\Delta\bar{\nu}$ | <i>n</i> | Δj | $\Delta\bar{\nu}$ |
| 0→0 | 3→1 | -587.3 | 0→0 | 2→0 | -351 |
| | 2→0 | -354.5 | | 0→2 | 356 |
| | 0→2 | 354.1 | | 1→3 | 587 |
| | 1→3 | 587.5 | 0→1 | 0→0 | 4156 |
| | 2→4 | 814.4 | | | |
| 3→5 | 1034.6 | | | | |
| 0→0 | 4162.1 | | | | |
| 1→1 | 4156.0 | | | | |
| 0→1 | 2→2 | 4144.8 | 1→1 | | |
| | 3→3 | 4126.9 | | | |
| | 0→2 | 4498.4 | | | |
| | 1→3 | 4713.3 | | | |
| | 2→4 | 4917.8 | | | |
| | 3→5 | 5109.8 | | | |
| | 2→0 | 3807.4 | | | |
| | 3→1 | 3568.9 | | | |

1274, calculated by Eucken (342) for a linear model of carbon dioxide.

The magnitude of the vibrational frequency shift for carbon monoxide as observed by Rasetti (361) and Bhagavantam (334), namely, $\Delta\bar{\nu}$ 2146, is indicative of the triple-bonded nature of the union between carbon and oxygen in this gas.

The Raman spectrum of ammonia has been investigated extensively. There are essentially three strong maxima in the liquids and in solution. These are, however, somewhat broad and diffuse and are somewhat reminiscent of the water bands.

In gaseous ammonia the central shift, $\Delta\bar{\nu}$ 3334, is reasonably sharp. Two lower frequency oscillations at $\Delta\bar{\nu}$ 934 and 964 have been observed by Amaldi and Placzek (324, 325). The three frequency shifts between $\Delta\bar{\nu}$ 1922 and 2270, also observed, are questionable. Rotational Raman spectra for ammonia gas have also been observed (325). The rotational $\Delta\bar{\nu}$ obtained are $\Delta\bar{\nu}$ 79, 99, 119, 140, 159, 179, 199, 219, 258, 298, and 336, as both Stokes and anti-Stokes lines. These correspond to transitions in which the rotational quantum number Δj changes by ± 1 as well as ± 2 and 0, which is compatible with the non-linear character of the molecule. Langseth (346) has analyzed the fine structure of the ammonium bands in concentrated solutions of ammonia and observed thirty-two lines occurring between $\Delta\bar{\nu}$ 3022 and $\Delta\bar{\nu}$ 3661, corresponding to the rotational-vibrational transitions in which the rotational quantum number changes by ± 1 or ± 2 , corresponding to the *O S* and *P R* branches, the *Q* branch being represented by the shift $\Delta\bar{\nu}$ 3312. This leads to a calculated moment of inertia of 2.8×10^{-40} g. cm.² for the molecule (346, 371).

It has been suggested that there may be some evidence of association of the ammonia molecule in liquid form (326, 338). This view was also held by Bhagavantam (226). It is predicated on a change in the relative intensities of the three higher frequency shifts with increasing temperature, $\Delta\bar{\nu}$ 3384 and 3212, becoming more feeble with an elevation in temperature. The shifts occurring at $\Delta\bar{\nu}$ 1070 and 1594 remain relatively constant and are attributed to characteristic oscillations of the ammonia molecule itself.

Aqueous solutions of ammonia give a Raman spectrum identical with that of the liquid itself. Investigations of solutions at various concentrations by Hollaender and Williams (343) and by Ricca (365), for example, show no evidence of the presence of an NH_4 ion as such. Aqueous solutions of ammonium salts, such as ammonium nitrate and ammonium chloride, show no Raman lines attributable to the NH_4 ion.

Two prominent frequency shifts are observed for nitrous oxide, $\Delta\bar{\nu}$ 1284 and 2224. The first of these is the stronger and is presumably attributable to a symmetrical oscillation. The remain-

ing shifts indicated in table 23 are very faint. From these Langseth and Nielsen (348) calculate a moment of inertia of 61×10^{-40} g. cm.² The structure of the molecule is linear and unsymmetrical, $\Delta\bar{\nu}$ 1284 corresponding to the oscillation $\overset{\rightarrow}{\text{N}} \text{N} \overset{\leftarrow}{\text{O}}$ and $\Delta\bar{\nu}$ 2224 to the oscillation $\overset{\rightarrow}{\text{N}} \overset{\leftarrow}{\text{N}} \overset{\rightarrow}{\text{O}}$ (327). The magnitude of the frequency shift would indicate the presence of a triple bond, and not the structure $\text{N}=\text{N}=\text{O}$ as it was formerly written. From a consideration of interatomic distances and moments of inertia of the molecule Pauling (357, 358) has recently come to the conclusion that the molecule resonates between several structures but that the effective binding over any period is $\text{N}\equiv\text{N}=\text{O}$. A similar resonance was also postulated for carbon monoxide, the triply bonded structure predominating.

Nitrogen peroxide (N_2O_4) has been included at this point because of its similar chemical composition to the other oxides of nitrogen. Menzies and Pringle (356) have observed $\Delta\bar{\nu}$ 275, which is considered an inactive fundamental. It is argued that if the molecule is linear, as presumed from x-ray analysis of NO_2 at -80°C ., the first vibration would be a symmetrical oscillation of the oxygen atoms about the stationary nitrogen atom analogous to that observed with nitrous oxide, and a faint line should be present corresponding to the unsymmetrical oscillation, both shifts being not greatly removed from those observed with nitrous oxide. No such lines were observed.

Not much can be said at this time regarding ozone or nitric oxide. Sutherland and Gerhard (370) have observed in ozone a very weak doublet corresponding to a mean frequency shift of $\Delta\bar{\nu}$ 1280. The weakness of the Raman spectrum is evidence against any simple symmetrical structure and suggests a non-equilateral triangular form of the molecule. Bhagavantam (334) has observed $\Delta\bar{\nu}$ 1877 in nitric oxide together with some unresolved rotational wings. Rasetti (101) has calculated the rotational transitions in nitric oxide.

Dadiou and Kohlrausch (232) have systematically investigated sulfur dioxide, hydrogen sulfide, and carbonyl sulfide, with the results given in table 25.

The frequency shifts from which these calculations may be made are given in table 23. The molecule, COS, is linear and unsymmetrical. The molecules SO₂ and H₂S are non-linear. The molecules CS₂ and CO₂ are both linear and symmetrical.

It might be mentioned that hydrogen sulfide shows a more marked change in its Raman shift in passing from the liquid to the gaseous state of aggregation than most substances. This difference is from $\Delta\bar{\nu}$ 2578 to $\Delta\bar{\nu}$ 2615. In most other compounds, where association plays no obvious rôle, the shifts are within a few wave numbers of each other in solid, liquid, or gaseous states where such data are available.

TABLE 25
Molecular constants calculated from the Raman effect

| SUBSTANCE | α | $s \times 10^8$ | $F \times 10^{-5}$ | $d \times 10^{-5}$ |
|-----------|----------|--------------------------|-----------------------|----------------------|
| O=C=O | 180° | cm. 0.98 | dynes per cm. 13.7 | dynes per cm. 1.2 |
| S=C=S | 180° | — | 6.9 (ca.) | 1.5 (?) |
| O=C=S | 180° | O...C 1.04 C...S 2.38 | 13.6 8.0 | 0.4 |
| O=S=O | 120° | 2.24 | 9.6 | 1.6 |
| H—S—H | 90° | 1.43 | 3.9 | 0.02 |
| S—H | — | 1.35 | 3.8 | — |

α = valence angle; s = interatomic distance from central atom; F = force constant in dynes per centimeter; d = deformation constant in dynes per centimeter.

The polymerization of sulfur trioxide and the absence of any Raman effect in aqueous solutions of hydrogen chloride have already been pointed out. As is to be expected, both liquid and gaseous hydrogen chloride have frequency shifts indicative of the homopolar nature of the binding under these conditions. This transition corresponds to the *Q* branch.

A series of experiments carried out by Bhagavantam (227, 83) on the effect of pressure on the rotational and vibrational Raman spectra of gases has led to interesting observations. It is presumed that the influence of neighboring molecules on Raman spectra may be attributed partly to a general intermolecular field and

partly to collisions. The mean frequency of collisions is a function of the pressure and the viscosity of the medium. As long as the pressure/viscosity ratio ($P\eta$) is small the perturbing influence of collisions on molecular rotation is small. By taking P/η to be equal to the frequency of rotation of the molecule in the one quantum state an estimate can be made of the pressures at which complete rotational quantization will no longer clearly exist. These can then be compared with the observed pressures at which discrete lines in the rotational Raman spectra fade and tend to become continuous. The observations yield the following results, the pressure being given in atmospheres:

| | <i>Calculated</i> | <i>Observed</i> |
|---------------------|-------------------|-----------------|
| Oxygen..... | 25 | 20-30 |
| Nitrogen..... | 29 | 30 |
| Carbon dioxide..... | 5 | 5 |

In some cases the observed rotational spectra diminish at pressures lower than the calculated pressure, and are attributed to the action of intermolecular fields.

Braune and Engelbrecht (230) have investigated a number of inorganic halides in the gaseous phase and compared the frequency shifts so obtained with those observable in liquid phase and in solution. The results in $\Delta\bar{\nu}$ are shown in table 26.

TABLE 26

| HALIDE | $\Delta\bar{\nu}$ | | |
|-------------------------|-------------------|------------|----------|
| | (gas) | (solution) | (liquid) |
| HgCl ₂ | 355 | 331 | 314 |
| HgBr ₂ | 220 | 205 | 195 |
| PCl ₃ | 523 | | 511 |
| AsCl ₃ | 422 | | 405 |
| SbCl ₃ | 382 | | 360 |
| AsBr ₃ | 287 | | 273 |

The frequency shifts observed in the gaseous state are greater in every case than the equivalent shift in the liquid, and this is attributed either to an increase in the binding forces through the action of adjacent molecules or to a decrease in the oscillating

mass on vaporization. With stannic chloride, however, two shifts are observed in the gas, $\Delta\bar{\nu}$ 367 and $\Delta\bar{\nu}$ 400, both closely corresponding to the shifts observed in the liquid. The percentage differences in the frequencies in the vapor and liquid states are approximately a linear function of the dipole moment. This is indicated in figure 17, where these differences are plotted against the observed and calculated moments. It is also observed that the inactive oscillation of the mercuric halides in the vapor state is proportional to their heat of dissociation.

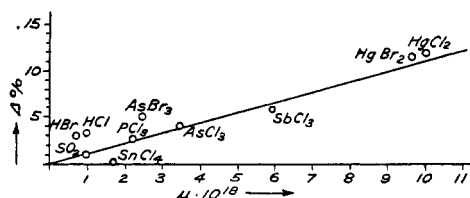


FIG. 17. PER CENT DIFFERENCE BETWEEN THE VAPOR AND LIQUID RAMAN SPECTRA OF SOME INORGANIC HALIDES PLOTTED AGAINST THE CALCULATED AND OBSERVED MOMENTS OF THESE COMPOUNDS

(After Braune and Engelbrecht)

XIII. CONCLUSION

It has been the purpose of this review to outline the interpretation, the development, and the application of Raman spectra, to collect, and to a certain extent to analyze, the data upon which such interpretations and applications are predicated. There are many fields which have not been explored. There are others which need further investigation. There are some contradictions and discrepancies. The contribution already made, however, to physics and chemistry by Raman spectra investigations is undisputed. The enormous progress already made in the five years since this discovery was announced speaks more eloquently than words as to its future utility.

REFERENCES

I. Introduction

- (1) BHAGAVANTAM: Indian J. Physics **5**, 257 (1930).
- (2) GANESAN: Indian J. Physics **4**, 281 (1930).
- (3) KOHLRAUSCH: Der Smekal-Raman Effekt. Verlag von Julius Springer, Berlin (1931).

- (4) MULLIKEN: Chem. Rev. **6**, 503 (1929).
- (5) MULLIKEN: Chem. Rev. **11**, 347 (1931).
- (6) SIRKAR: Indian J. Physics **7**, 431 (1932).
- (7) VILLARS: Chem. Rev. **12**, 369 (1932).

II. Theory

- (8) ANDREWS: Proc. Roy. Acad. Amsterdam **29**, 744 (1926).
- (9) ANDREWS: Chem. Rev. **5**, 533 (1928).
- (10) ANDREWS: Phys. Rev. **34**, 1626 (1929).
- (11) ANDREWS: Phys. Rev. **36**, 544 (1930).
- (12) BÄR: Helv. Phys. Acta **4**, 130 (1931).
- (13) BATES AND ANDREWS: Proc. Nat. Acad. Sci. **14**, 124 (1928).
- (14) BHAGAVANTAM: Indian J. Physics **5**, 73 (1930).
- (15) BHAGAVANTAM: Indian J. Physics **7**, 79 (1932).
- (16) BHAGAVANTAM AND VENKATESWARAN: Nature **129**, 580 (1932).
- (17) BJERRUM. Ber. deut. physik. Ges. **16**, 737 (1914).
- (18) BRICKWEDDE AND PETERS: Phys. Rev. **33**, 116 (1929).
- (19) CABANNES: Compt. rend. **186**, 1201 (1928).
- (20) CABANNES: Compt. rend. **194**, 2134 (1932).
- (21) CABANNES AND ROUSSET: Compt. rend. **194**, 79 (1932).
- (22) CABANNES AND ROUSSET: Ann. phys. **19**, 229 (1933).
- (23) DAURE: Compt. rend. **188**, 1605 (1929).
- (24) DAURE: Ann. phys. **12**, 375 (1929).
- (25) DENNISON: Astrophys. J. **62**, 84 (1925).
- (26) DENNISON: Phil. Mag. [7] **1**, 195 (1926).
- (27) DIEKE: Nature **123**, 564 (1929).
- (28) ELLENBERGER: Ann. Physik **14**, 221 (1932).
- (29) ELLIS: J. Franklin Inst. **208**, 517 (1929).
- (30) KASTLER: Compt. rend. **192**, 1032 (1931).
- (31) KETTERING, SHUTTS, AND ANDREWS: Phys. Rev. **36**, 531 (1930).
- (32) KOHLRAUSCH: Reference 3, p. 171.
- (33) Reference 3, p. 173.
- (34) Reference 3, p. 176.
- (35) KRAMERS AND HEISENBERG: Z. Physik **31**, 681 (1925).
- (36) KRISHNAN: Nature **122**, 650 (1928).
- (37) LANDSBERG AND MANDELSTAM: Naturwissenschaften **16**, 557 (1928).
- (38) LANDSBERG AND MANDELSTAM: Naturwissenschaften **16**, 772 (1928).
- (39) LANDSBERG AND MANDELSTAM: Z. Physik **65**, 719 (1930).
- (40) LANGER: Nature **123**, 345 (1929).
- (41) LANGER AND MEGGERS: Phys. Rev. **33**, 115 (1929).
- (42) LECHNER: Sitzber. Akad. Wiss. Wien, Abt. IIb, **141**, 291 (1932).
- (43) LESPIEAU, BORGUEL, AND WAKEMAN: Bull. soc. chim. **51**, 400 (1932).
- (44) LINDEMANN: Physik. Z. **11**, 609 (1910).
- (45) MANNEBACK: Z. Physik **62**, 224 (1930).
- (46) MANNEBACK: Z. Physik **65**, 574 (1930).
- (47) NEY: Z. Physik **68**, 554 (1931).
- (48) ORNSTEIN AND REKVELD: Z. Physik **57**, 539 (1929).
- (49) ORNSTEIN AND REKVELD: Z. Physik **61**, 593 (1930).

- (50) ORNSTEIN AND REKVELD: *Z. Physik* **68**, 257 (1931).
- (51) ORNSTEIN, WENT, AND ATEN: *Z. Physik* **82**, 750 (1933).
- (52) PARAMASIVAN: *Indian J. Physics* **6**, 413 (1931).
- (53) PAULING: *J. Am. Chem. Soc.* **54**, 988 (1932).
- (54) PLACZEK: *Z. Physik* **58**, 585 (1929).
- (55) RAMAN: *Indian J. Physics* **2**, 387 (1928).
- (56) RADAKOVIC: *Sitzber. Akad. Wiss. Wien, Abt. IIb*, **139**, 107 (1930).
- (57) RADAKOVIC: *Sitzber. Akad. Wiss. Wien, Abt. IIb*, **141**, 41 (1932).
- (58) RASETTI: *Nature* **123**, 757 (1929).
- (59) ROCARD: *Compt. rend.* **186**, 1107 (1928).
- (60) SALANT: *Proc. Nat. Acad. Sci.* **12**, 334 (1926).
- (61) SALANT: *Proc. Nat. Acad. Sci.* **12**, 370 (1926).
- (62) SEGRÉ: *Nuovo cimento* **7**, 380 (1930).
- (63) SIRKAR: *Indian J. Physics* **5**, 159 (1930).
- (64) SIRKAR: *Indian J. Physics* **5**, 593 (1930).
- (65) SIRKAR: *Indian J. Physics* **6**, 133 (1931).
- (66) SIRKAR: *Indian J. Physics* **6**, 295 (1931).
- (67) SMEKAL: *Naturwissenschaften* **11**, 873 (1923).
- (68) SPECCHIA: *Nuovo cimento* **9**, 133 (1932).
- (69) TRUMPY: *Z. Physik* **62**, 806 (1930).
- (70) VAN VLECK: *Proc. Nat. Acad. Sci.* **15**, 754 (1929).
- (71) VENKATESACHAR AND SIBAIYA: *Indian J. Physics* **5**, 747 (1930).
- (72) WEILER: *Z. Physik* **68**, 782 (1931).
- (73) WEILER: *Z. Physik* **72**, 206 (1931).
- (74) WERTH: *Phys. Rev.* **39**, 299 (1932).
- (75) YATES: *Phys. Rev.* **36**, 563 (1930).
- (76) YATES: *Phys. Rev.* **36**, 555 (1930).
- (77) YATES: *Phys. Rev.* **37**, 616 (1931).

III. Technique

- (78) ALMASY: *Physik. Z.* **33**, 221 (1932).
- (79) ANAND: *J. Sci. Instruments* **8**, 258 (1931).
- (80) ANAND: *J. Sci. Instruments* **9**, 324 (1932).
- (81) BÄR: *Helv. Phys. Acta* **5**, 174 (1932).
- (82) BATES AND TAYLOR: *J. Am. Chem. Soc.* **50**, 771 (1928).
- (83) BHAGAVANTAM: *Indian J. Physics* **6**, 319 (1931).
- (84) BOLLA: *Nuovo cimento* **9**, 290 (1932).
- (85) BOURGUEL: *Rev. optique* **10**, 474 (1931).
- (86) BUTTOLPH: *Rev. Sci. Instruments* **1**, 650 (1930).
- (87) DANIELS AND HEIDT: *J. Am. Chem. Soc.* **54**, 2381 (1932).
- (88) GRASSMANN: *Z. Physik* **72**, 240 (1931).
- (89) HIBBEN: To be published.
- (90) HIGH AND POOL: *Phys. Rev.* **38**, 374 (1931).
- (91) HOFFMAN AND DANIELS: *J. Am. Chem. Soc.* **54**, 4226 (1932).
- (92) HULUBEI: *Compt. rend.* **194**, 1474 (1932).
- (93) HULUBEI AND CAUCHOIS: *Compt. rend.* **192**, 935 (1931).
- (94) HULUBEI AND CAUCHOIS: *Compt. rend.* **192**, 1640 (1931).
- (95) KRISHNAMURTI: *Indian J. Physics* **5**, 587 (1930).

- (96) KRISHNAMURTI: Indian J. Physics **5**, 651 (1930).
- (97) MCLENNAN, SMITH, AND WILHELM: Trans. Roy. Soc. Can. **23**, 247 (1929).
- (98) MESNAGE: J. phys. radium [7] **2**, 403 (1931).
- (99) NIELSEN: J. Optical Soc. Am. **20**, 701 (1930).
- (100) PFUND: Phys. Rev. **42**, 581 (1932).
- (101) RASETTI: Nuovo cimento **7**, 261 (1930).
- (102) TAYLOR AND BATES: Proc. Nat. Acad. Sci. **12**, 714 (1926).
- (103) WOOD: PHIL. Mag. [7] **7**, 858 (1928).
- (104) WOOD: Phys. Rev. **33**, 294 (1929).
- (105) WOOD: Phys. Rev. **33**, 1097 (1929).
- (106) WOOD: Phys. Rev. **36**, 1421 (1930).
- (107) WOOD: Phys. Rev. **37**, 1022 (1931).
- (108) WOOD: Phys. Rev. **38**, 2168 (1931).
- (109) ZIEMECKI: Bull. intern. acad. polonaise, p. 309 (1930).

IV. Crystals

- (110) BÄR: Nature **124**, 692 (1929).
- (111) BHAGAVANTAM: Indian J. Physics **5**, 35 (1930).
- (112) BHAGAVANTAM: Z. Krist. **77**, 43 (1931).
- (113) CABANNES: Compt. rend. **195**, 1353 (1932).
- (114) CABANNES AND CANALS: Compt. rend. **193**, 289 (1931).
- (115) CABANNES AND OSBORNE: Compt. rend. **193**, 156 (1931).
- (116) CARRELLI, PRINGSHEIM, AND ROSEN: Z. Physik **51**,¹/₂511 (1928).
- (117) EMBIRIKOS: Z. Physik **65**, 266 (1930).
- (118) FERMI: Mem. Italia Fis. **3**, 5 (1932).
- (119) FERMI AND RASETTI: Z. Physik **71**, 689 (1931).
- (120) GERLACH: Ann. Physik **5**, 196 (1930).
- (121) GOPAL PAI: Indian J. Physics **7**, 285 (1932).
- (122) GROSS AND ROMANOVA: Z. Physik **55**, 744 (1929).
- (123) HAUN AND HARKINS: J. Am. Chem. Soc. **54**, 3917 (1932).
- (124) HIBBEN: J. Am. Chem. Soc. **53**, 2418 (1931).
- (125) HIBBEN: Proc. Nat. Acad. Sci. **18**, 532 (1932).
- (126) HOLLAENDER AND WILLIAMS: Phys. Rev. **34**, 380 (1929).
- (127) HOLLAENDER AND WILLIAMS: Phys. Rev. **38**, 1739 (1931).
- (128) KIMURA AND UCHIDA: Japan. J. Physics **5**, 97 (1928).
- (129) KIMURA AND UCHIDA: Sci. Papers Inst. Phys. Chem. Research Tokyo **11**, 199 (1929).
- (130) KRISHNAMURTI: Indian J. Physics **5**, 1 (1930).
- (131) KRISHNAMURTI: Indian J. Physics **5**, 105 (1930).
- (132) KRISHNAMURTI: Indian J. Physics **5**, 113 (1930).
- (133) KRISHNAMURTI: Indian J. Physics **5**, 183 (1930).
- (134) KRISHNAMURTI: Indian J. Physics **5**, 633 (1930).
- (135) KRISHNAMURTI: Nature **125**, 463 (1930).
- (136) KRISHNAMURTI: Indian J. Physics **6**, 7 (1931).
- (137) KRISHNAMURTI: Nature **126**, 169 (1931).
- (138) KRISHNAN: Nature **122**, 477 (1928).
- (139) KRISHNAN: Indian J. Physics **4**, 131 (1929).
- (140) LANDSBERG AND MANDELSTAM: Compt. rend. **187**, 109 (1928).

- (141) LANDSBERG AND MANDELSTAM: *Z. Physik* **50**, 769 (1928).
- (142) MENZIES: *Nature* **124**, 511 (1929).
- (143) MENZIES: *Phil. Mag.* **8**, 504 (1929).
- (144) NISI: *Proc. Imp. Acad. Tokyo* **5**, 127 (1929).
- (145) NISI: *Proc. Imp. Acad. Tokyo* **5**, 407 (1929).
- (146) NISI: *Japan. J. Physics* **7**, 1 (1931).
- (147) NISI: *Proc. Phys. Math. Soc. Japan, Series 3*, **14**, 214 (1932).
- (148) NISI: *Proc. Phys. Math. Soc. Japan, Series 3*, **15**, 114 (1933).
- (149) PRINGSHEIM AND ROSEN: *Z. Physik* **50**, 741 (1928).
- (150) RAO: *Indian J. Physics* **3**, 123 (1928).
- (151) RASETTI: *Nature* **127**, 626 (1931).
- (152) RASETTI: *Nuovo cimento* **8**, Rivista 89 (1931).
- (153) RASETTI: *Nuovo cimento* **9**, 72 (1932).
- (154) REDLICH: *Naturwissenschaften* **20**, 365 (1932).
- (155) SCHAEFER, MATOSI, AND ADERHOLD: *Physik. Z.* **30**, 581 (1929).
- (156) SCHAEFER, MATOSI, AND ADERHOLD: *Z. Physik* **65**, 289 (1930).
- (157) TOMASCHEK: *Nature* **128**, 495 (1931).
- (158) WEILER: *Nature* **130**, 893 (1932).
- (159) WEILER: *Helv. Phys. Acta* **5**, 302 (1932).
- (160) WEILER: *Z. Physik* **80**, 617 (1933).
- (161) WOOD: *Phil. Mag.* **6**, 729 (1928).

V. Water

- (162) BOLLA: *Nature* **128**, 546 (1931).
- (163) BOLLA: *Nuovo cimento* **10**, 101 (1933).
- (164) BRUNETTI AND OLLANO: *Atti accad. Lincei* **12**, 522 (1930).
- (165) DAURE AND KASTLER: *Compt. rend.* **192**, 1721 (1931).
- (166) GANESAN AND VENKATESWARAN: *Indian J. Physics* **4**, 195 (1930).
- (167) GERLACH: *Naturwissenschaften* **18**, 68 (1930).
- (168) HATLEY AND CALLIHAN: *Phys. Rev.* **33**, 909 (1931).
- (169) JOHNSTON AND WALKER: *Phys. Rev.* **39**, 535 (1932).
- (170) MAGAT: *Compt. rend.* **196**, 1981 (1933).
- (171) MECKE: *Z. physik. Chem.* **16**, 431 (1932).
- (172) MECKE, BAUMANN, AND FREUDENBERG: *Z. Physik* **81**, 313 (1933).
- (173) MECKE, BAUMANN, AND FREUDENBERG: *Z. Physik* **81**, 445 (1933).
- (174) MECKE, BAUMANN, AND FREUDENBERG: *Z. Physik* **81**, 465 (1933).
- (175) MEYER: *Physik. Z.* **31**, 510 (1930).
- (176) NISI: *Japan. J. Physics* **7**, 27 (1931).
- (177) OLLANO: *Z. Physik* **77**, 818 (1932).
- (178) PRINGSHEIM AND SCHLIVITCH: *Z. Physik* **60**, 581 (1930).
- (179) RAFALOWSKI: *Nature* **128**, 546 (1931).
- (180) RANK: *J. Chem. Physics* **1**, 504 (1933).
- (181) RAO: *Nature* **125**, 600 (1930).
- (182) RAO: *Proc. Roy. Soc. London* **130**, 489 (1931).
- (183) SEGRÉ: *Atti accad. Lincei* **13**, 929 (1931).
- (184) SILVEIRA: *Compt. rend.* **195**, 652 (1932).
- (185) SPECCHIA: *Nuovo cimento* **7**, 388 (1930).

- (186) SPECCHIA: *Atti accad. Lincei* **12**, 659 (1930).
(187) VAN VLECK AND CROSS: *J. Chem. Physics* **1**, 357 (1933).

VI. Acids and bases

- (188) ANTHONY AND HUDLESTON: *J. Chem. Soc.* **127**, 1122 (1925).
(189) BÄR: *Z. Physik* **79**, 455 (1932).
(190) BELL AND FREDRICKSON: *Phys. Rev.* **37**, 1562 (1931).
(191) BRUNETTI AND OLLANO: *Atti accad. Lincei* **13**, 52 (1931).
(192) BRUNETTI AND OLLANO: *Nuovo cimento* **8**, 169 (1931).
(193) DADIEU AND KOHLRAUSCH: *J. Optical Soc. Am.* **5**, 286 (1931).
(194) DADIEU AND KOHLRAUSCH: *Naturwissenschaften* **19**, 690 (1931).
(195) DAVIES AND HUDLESTON: *J. Chem. Soc.* **125**, 260 (1924).
(196) DICKINSON AND DILLON: *Proc. Nat. Acad. Sci.* **15**, 334 (1929).
(197) DICKINSON AND WEST: *Phys. Rev.* **35**, 1126 (1930).
(198) FADDA: *Nuovo cimento* **9**, 168 (1932).
(199) GHOSH AND DAS: *J. Phys. Chem.* **36**, 586 (1932).
(200) HANTZSCH: *Z. Physik. Chem.* **134**, 406 (1928).
(201) HANTZSCH: *Z. Elektrochem.* **31**, 167 (1925).
(202) HARKINS, GANS, AND BOWERS: *Nature* **125**, 464 (1930).
(203) HULUBEI AND CAUCHOIS: *Compt. rend.* **192**, 1640 (1931).
(204) KINSEY: *Phys. Rev.* **35**, 284 (1930).
(205) KRISHNAMURTI: *Indian J. Physics* **6**, 345 (1931).
(206) MECKE: *Leipziger Vorträge*, p. 23 (1931).
(207) NIELSEN: *Z. Physik* **76**, 55 (1932).
(208) NISI: *Japan. J. Physics* **5**, 119 (1929).
(209) NISI: *Japan. J. Physics* **6**, 1 (1930).
(210) OLLANO: *Nuovo cimento* **9**, 51 (1932).
(211) OLLANO: *Nuovo cimento* **9**, 264 (1932).
(212) PRINGSHEIM AND YOST: *Z. Physik* **58**, 1 (1929).
(213) RAO: *Proc. Roy. Soc. London* **127**, 279 (1930).
(214) RAO: *Proc. Roy. Acad. Amsterdam* **33**, 112 (1930).
(215) RICCA: *Atti accad. Lincei* **14**, 288 (1931).
(216) SALANT AND SANDOW: *Phys. Rev.* **35**, 214 (1930).
(217) SCHAEFER AND SCHUBERT: *Ann. Physik* **50**, 283 (1916).
(218) SPECCHIA: *Atti accad. Lincei* **13**, 754 (1931).
(219) TAYLOR: *Trans. Faraday Soc.* **25**, 830 (1929).
(220) THOMPSON AND NIELSEN: *Phys. Rev.* **37**, 1669 (1931).
(221) WAWILOW AND TUMMERMANN: *Z. Physik* **54**, 270 (1929).
(222) WOOD AND DIEKE: *Phys. Rev.* **35**, 1355 (1930).
(223) WOODWARD: *Physik. Z.* **32**, 212 (1931).
(224) WOODWARD: *Physik. Z.* **32**, 261 (1931).
(225) WOODWARD: *Physik. Z.* **32**, 777 (1931).

VII. Solutions

- (226) BHAGAVANTAM: *Indian J. Physics* **5**, 49 (1930).
(227) BHAGAVANTAM: *Indian J. Physics* **5**, 59 (1930).
(228) BRAUNE AND ENGELBRECHT: *Z. physik. Chem.* **B10**, 1 (1930).
(229) BRAUNE AND ENGELBRECHT: *Z. physik. Chem.* **B11**, 409 (1931).

- (230) BRAUNE AND ENGELBRECHT: *Z. physik. Chem.* **B19**, 303 (1932).
(231) DADIEU, JELE, AND KOHLRAUSCH: *Sitzber. Akad. Wiss. Wien, Abt. IIb*, **140**, 293 (1931).
(232) DADIEU AND KOHLRAUSCH: *Physik. Z.* **33**, 165 (1932).
(233) DAMASCHUN: *Z. physik. Chem.* **16**, 81 (1932).
(234) DAURE: *Compt. rend.* **186**, 1833 (1928).
(235) DAURE: *Compt. rend.* **187**, 940 (1928).
(236) FADDA: *Nuovo cimento* **9**, 227 (1932).
(237) FOERSTER, BROSCHE, AND NORBERG-SCHULZ: *Z. physik. Chem.* **110**, 435 (1924).
(238) GRASSMANN: *Z. Physik* **77**, 616 (1932).
(239) GRASSMANN: *Naturwissenschaften* **20**, 560 (1932).
(240) GRASSMANN: *Z. Physik* **82**, 765 (1933).
(241) HOLLAENDER AND WILLIAMS: *Phys. Rev.* **34**, 994 (1929).
(242) JONES: *Z. physik. Chem.* **11**, 539 (1893).
(243) KISHI: *MEM. Coll. Sci. Kyoto Imp. Univ., Series A*, **13**, 163 (1930).
(244) LEONTOWITSCH: *Z. Physik* **54**, 155 (1929).
(245) MELLOR: *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. V. Longmans, Green and Co., London (1924).
(246) MELLOR: *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. V, p. 311. Longmans, Green and Co., London (1924).
(247) MUKHERJEE AND SEN GUPTA: *Indian J. Physics* **3**, 503 (1929).
(248) MUSPRATT: *Ann.* **50**, 259 (1844).
(249) MUSPRATT: *Ann.* **64**, 240 (1845).
(250) NOYES: *Z. physik. Chem.* **9**, 619 (1892).
(251) RAMASWAMY: *Indian J. Physics* **5**, 193 (1930).
(252) SCHULZE: *Z. Elektrochem.* **28**, 387 (1922).
(253) SIDGWICK: *Electron Theory of Valency*, p. 175. Oxford University Press (1929).
(254) SILVEIRA: *Compt. rend.* **194**, 1336 (1932).
(255) SILVEIRA: *Compt. rend.* **195**, 521 (1932).
(256) SILVEIRA AND BAUER: *Compt. rend.* **195**, 416 (1932).
(257) STERLING AND LAIRD: *Phys. Rev.* **36**, 149 (1930).
(258) TRUMPY: *Kgl. Norske Videnskab. Selskabs Forh.* **III**, 159 (1931).
(259) VENKATESWARAN: *Nature* **127**, 406 (1931).
(260) VENKATESWARAN: *Indian J. Physics* **6**, 51 (1931).
(261) WOODWARD: *Physik. Z.* **31**, 792 (1930).
(262) WYCKOFF: *The Structure of Crystals*, chap. 18. The Chemical Catalog Co., New York (1931).

VIII. Complex compounds

- (263) BOSE AND DATTA: *Nature* **128**, 725 (1931).
(264) GERLACH: *Sitzber. math. naturw. Abt. bayer. Akad. Wiss. München*, p. 39 (1932).
(265) JOOS AND DAMASCHUN: *Z. Physik* **32**, 553 (1931).
(266) KRACEK: *J. Phys. Chem.* **34**, 225 (1930).
(267) KRACEK, BARTH, AND KSANDA: *Phys. Rev.* **40**, 1034 (1932).
(268) SAMUEL AND KHAN: *Z. Physik* **84**, 87 (1933).

- (269) STEWART: *Phys. Rev.* **43**, 1057 (1933).
(270) TRUMPY: *Z. Physik* **68**, 675 (1931).
(271) TRUMPY: *Kgl. Norske Videnskab. Selskabs Forh.* IV, 102 (1931).

IX. Amorphous compounds

- (272) BHAGAVANTAM: *Indian J. Physics* **6**, 1 (1931).
(273) BRAGG AND GIBBS: *Proc. Roy. Soc. London* **A109**, 405 (1925).
(274) EULITZ: *Z. Krist.* **80**, 208 (1931).
(275) KONRAD, BACHLE, AND SIGNER: *Ann.* **473**, 276 (1929).
(276) SIGNER AND WEILER: *Helv. Chim. Acta* **16**, 115 (1933).
(277) STAUDINGER: *Ann.* **473**, 272 (1929).
(278) WYCKOFF: *Z. Krist.* **62**, 189 (1925).

X. Liquids

- (279) BHAGAVANTAM: *Nature* **126**, 995 (1930).
(280) BHAGAVANTAM: *Phys. Rev.* **39**, 1020 (1932).
(281) BHAGAVANTAM: *Nature* **129**, 167 (1932).
(282) BRADLEY: *Phys. Rev.* **40**, 908 (1932).
(283) BRUNI AND AMODORI: *Atti accad. Lincei* **28**, I, 217 (1919).
(284) CABANNES: *Trans. Faraday Soc.* **25**, 194 (1929).
(285) CABANNES: *Trans. Faraday Soc.* **25**, 813 (1929).
(286) DAURE: *Compt. rend.* **187**, 826 (1928).
(287) DAURE: *Compt. rend.* **188**, 61 (1929).
(288) GANESAN AND VENKATESWARAN: *Nature* **124**, 57 (1929).
(289) HANLE: *Ann. Physik* **15**, 345 (1932).
(290) HEMPTINNE: *Ann. soc. sci. Bruxelles, Series B*, 185 (1932).
(291) LANGSETH: *Z. Physik* **72**, 350 (1931).
(292) MATOSI AND ADERHOLD: *Z. Physik* **68**, 683 (1931).
(293) MEYER: *Z. anorg. Chem.* **203**, 146 (1931).
(294) MICHAELIS AND SCHIFFERDECKER: *Ber.* **6**, 993 (1873).
(295) PETRIKALN: *Z. physik. Chem.* **3**, 360 (1929).
(296) PETRIKALN AND HOCHBERG: *Z. physik. Chem.* **3**, 217 (1929).
(297) PETRIKALN AND HOCHBERG: *Z. physik. Chem.* **3**, 405 (1929).
(298) PETRIKALN AND HOCHBERG: *Z. physik. Chem.* **4**, 299 (1929).
(299) RAMAN AND KRISHNAN: *Nature* **122**, 882 (1928).
(300) SCHAEFER: *Z. Physik* **60**, 586 (1930).
(301) SUGDEN: *Parachor and Valency*, p. 188. Alfred Knopf, New York (1930).
(302) THORPE: *J. Chem. Soc.* **37**, 141 (1880).
(303) THORPE: *J. Chem. Soc.* **37**, 327 (1880).
(304) TRUMPY: *Z. Physik* **66**, 790 (1930).
(305) UREY AND BRADLEY: *Phys. Rev.* **37**, 843 (1931).
(306) VENKATESWARAN: *Indian J. Physics* **6**, 275 (1931).
(307) VENKATESWARAN: *Nature* **128**, 870 (1931).

XI. Cyanogen compounds

- (308) DADIEU: *Naturwissenschaften* **18**, 895 (1930).
(309) DADIEU: *Sitzber. Akad. Wiss. Wien, Abt. IIb*, **139**, 629 (1930).
(310) DADIEU: *Monatsh.* **57**, 437 (1931).

- (311) DADIEU: Ber. **64**, 358 (1931).
- (312) DADIEU AND KOHLRAUSCH: Ber. **63**, 1657 (1930).
- (313) DADIEU AND KOHLRAUSCH: Sitzber. Akad. Wiss. Wien, Abt. IIb, **139**, 77 (1930).
- (314) DADIEU AND KOHLRAUSCH: Monatsh. **55**, 379 (1930).
- (315) KASTLER: Compt. rend. **194**, 858 (1932).
- (316) PAL AND SEN GUPTA: Indian J. Physics **5**, 13 (1930).
- (317) PAL AND SEN GUPTA: Indian J. Physics **5**, 611 (1930).
- (318) PETRIKALN AND HOCHBERG: Z. physik. Chem. **8**, 440 (1930).
- (319) PRINGSHEIM: Naturwissenschaften **16**, 597 (1928).
- (320) SMYTH: Dielectric Constant and Molecular Structure, p. 85. The Chemical Catalog Co., New York (1931).
- (321) SUGDEN: Parachor and Valency, p. 38. Alfred Knopf, New York (1930).
- (322) SUGDEN: Parachor and Valency, p. 171. Alfred Knopf, New York (1930).
- (323) WEST AND FARNSWORTH: J. Chem. Physics **1**, 402 (1933).

XII. Gases

- (324) AMALDI AND PLACZEK: Naturwissenschaften **20**, 521 (1932).
- (325) AMALDI AND PLACZEK: Z. Physik **81**, 259 (1933).
- (326) AUSTIN: Nature **125**, 464 (1930).
- (327) BARKER: Nature **129**, 132 (1932).
- (328) BHAGAVANTAM: Nature **126**, 502 (1930).
- (329) BHAGAVANTAM: Nature **127**, 817 (1931).
- (330) BHAGAVANTAM: Nature **128**, 70 (1931).
- (331) BHAGAVANTAM: Nature **128**, 188 (1931).
- (332) BHAGAVANTAM: Nature **128**, 272 (1931).
- (333) BHAGAVANTAM: Indian J. Physics **7**, 107 (1932).
- (334) BHAGAVANTAM: Phys. Rev. **42**, 437 (1932).
- (335) BHAGAVANTAM: Current Sci. **1**, 9 (1932).
- (336) BHAGAVANTAM: Indian J. Physics **7**, 549 (1933).
- (337) DADIEU AND KOHLRAUSCH: Sitzber. Akad. Wiss. Wien, "Abt. IIb, **139**, 717 (1930).
- (338) DADIEU AND KOHLRAUSCH: Naturwissenschaften **18**, 154 (1930).
- (339) DADIEU AND KOHLRAUSCH: Monatsh. **57**, 488 (1931).
- (340) DAURE: Trans. Faraday Soc. **25**, 825 (1929).
- (341) DICKINSON, DILLON, AND RASETTI: Phys. Rev. **34**, 582 (1929).
- (342) EUCKEN: Z. Physik **37**, 714 (1927).
- (343) HOLLAENDER AND WILLIAMS: Phys. Rev. **37**, 1367 (1931).
- (344) HOUSTON AND LEWIS: Proc. Nat. Acad. Sci. **17**, 229 (1931).
- (345) HOUSTON AND LEWIS: Phys. Rev. **37**, 227 (1931).
- (346) LANGSETH: Z. Physik **77**, 60 (1932).
- (347) LANGSETH AND NIELSEN: Z. physik. Chem. **19**, 427 (1932).
- (348) LANGSETH AND NIELSEN: Nature **130**, 92 (1932).
- (349) McLENNAN: Trans. Faraday Soc. **25**, 797 (1929).
- (350) McLENNAN AND McLEOD: Trans. Roy. Soc. Can. **22**, 413 (1928).
- (351) McLENNAN AND McLEOD: Nature **123**, 160 (1929).
- (352) McLENNAN AND McLEOD: Trans. Roy. Soc. Can. **23**, 19 (1929).
- (353) McLENNAN AND SMITH: Can. J. Research **7**, 551 (1932).

- (354) McLENNAN, SMITH, AND WILHELM: *Trans. Roy. Soc. Can.* **23**, 279 (1929).
(355) McLENNAN, SMITH, AND WILHELM: *Trans. Roy. Soc. Can.* **24**, 197 (1930).
(356) MENZIES AND PRINGLE: *Nature* **127**, 707 (1931).
(357) PAULING: *Proc. Nat. Acad. Sci.* **18**, 293 (1932).
(358) PAULING: *Proc. Nat. Acad. Sci.* **18**, 498 (1932).
(359) RASETTI: *Nature* **123**, 160 (1929).
(360) RASETTI: *Phys. Rev.* **34**, 367 (1929).
(361) RASETTI: *Nature* **123**, 205 (1929).
(362) RASETTI: *Nature* **124**, 93 (1929).
(363) RASETTI: *Proc. Nat. Acad. Sci.* **15**, 234 (1929).
(364) RASETTI: *Nuovo cimento* **6**, 356 (1929).
(365) RICCA: *Atti accad. Lincei* **14**, 197 (1931).
(365a) SALANT AND CALLIHAN: *Phys. Rev.* **43**, 590 (1933).
(366) SALANT AND SANDOW: *Phys. Rev.* **33**, 1096 (1929).
(367) SALANT AND SANDOW: *Phys. Rev.* **36**, 1591 (1930).
(368) SALANT AND SANDOW: *Phys. Rev.* **37**, 373 (1931).
(369) SEGRÉ: *Atti accad. Lincei* **11**, 825 (1930).
(370) SUTHERLAND AND GERHARD: *Nature* **130**, 241 (1932).
(371) WILLIAMS AND HOLLAENDER: *Phys. Rev.* **42**, 379 (1932).
(372) WOOD: *Phil. Mag.* **7**, 744 (1929).
(373) WOOD: *Nature* **123**, 166 (1929).
(374) WOOD: *Nature* **123**, 279 (1929).

SUPPLEMENTARY REFERENCES²*II. Theory*

- AMALDI AND SEGRÉ: *Atti accad. Lincei* [6] **9**, 407 (1929).
BAILEY: *Phil. Mag.* **13**, 993 (1932).
BHAGAVANTAM: *Indian J. Physics* **6**, 331 (1931).
BHAGAVANTAM: *Indian J. Physics* **6**, 389 (1931).
BHAGAVANTAM: *Indian J. Physics* **6**, 557 (1932).
CABANNES: *Compt. rend.* **191**, 1123 (1930).
CABANNES: *J. phys. radium* [7] **2**, 381 (1931).
CABANNES AND OSBORNE: *Compt. rend.* **193**, 1410 (1931).
CABANNES AND ROUSSET: *Compt. rend.* **194**, 706 (1932).
CARRELLI AND WENT: *Z. Physik* **76**, 236 (1932).
COTTON: *Compt. rend.* **193**, 1078 (1931).
DESLANDRES: *Compt. rend.* **193**, 1364 (1931).
DESLANDRES: *Compt. rend.* **194**, 2093 (1932).
GANGULI: *Phil. Mag.* **13**, 306 (1932).
GOLDSTEIN: *Compt. rend.* **195**, 703 (1932).

² The references given in the supplementary bibliography include: (a) references in journals not readily available; (b) references by the same author which practically duplicate a reference cited in the text; (c) references which are not entirely pertinent to the material discussed in the text; (d) a few references which came to the attention of the reviewer too late to be included in the discussion of the text.

- GROSS AND KHVOSTIKOV: Phys. Rev. **42**, 579 (1932).
 HANLE: Naturwissenschaften **19**, 375 (1931).
 HANLE: Physik. Z. **32**, 556 (1931).
 HANLE: Ann. Physik **11**, 885 (1931).
 HILL AND KEMBLE: Proc. Nat. Acad. Sci. **15**, 387 (1929).
 KAST AND WURSTLIN: Physik. Z. **81**, 581 (1933).
 KASTLER: Compt. rend. **191**, 565 (1930).
 KASTLER: Compt. rend. **193**, 1075 (1931).
 KEMBLE AND HILL: Phys. Rev. **33**, 1096 (1929).
 KOHLRAUSCH: Z. physik. Chem. **B18**, 61 (1932).
 LANDSBERG AND MANDELSTAM: Z. Physik **73**, 502 (1931).
 LEONTOWITSCH: Physik. Z. Sowjetunion **1**, 317 (1932).
 LINDSAY: Nature **127**, 305 (1931).
 LOOMIS AND WINANS: Z. Physik **73**, 658 (1931).
 MATOSSI: Z. Physik **64**, 34 (1930).
 MECKE: Z. Physik **64**, 173 (1930).
 MECKE: Z. physik. Chem. **B17**, 1 (1932).
 MENZIES: Trans. Faraday Soc. **25**, 836 (1929).
 MENZIES: Proc. Roy. Soc. London **134**, 265 (1931).
 NEY: Compt. rend. soc. phys. Warsaw **5**, 389 (1931).
 ORNSTEIN AND REKVELD: Z. Physik **65**, 719 (1930).
 PLACZEK: Z. Physik **70**, 84 (1931).
 PLACZEK: Leipziger Vorträge, p. 71 (1931).
 PLACZEK: Nature **128**, 410 (1931).
 PLACZEK AND VAN WIJK: Z. Physik **67**, 582 (1931).
 RADAKOVIC: Monatsh. **60**, 239 (1932).
 RAMAN: Nature **128**, 545 (1931).
 RAMAN AND BHAGAVANTAM: Nature **128**, 114 (1931).
 RAMAN AND BHAGAVANTAM: Indian J. Physics **6**, 353 (1931).
 RAMAN AND BHAGAVANTAM: Nature **128**, 727 (1931).
 RAMAN AND BHAGAVANTAM: Nature **129**, 22 (1932).
 RASETTI: Leipziger Vorträge, p. 59 (1931).
 RAY-CHAUDHURI: Z. Physik **72**, 242 (1931).
 RAY-CHAUDHURI: Z. Physik **74**, 574 (1932).
 REDLICH, KURZ, AND ROSENFELD: Z. physik. Chem. **B19**, 231 (1932).
 REKVELD: Arch. néerland. sci [IIIA] **13**, 73 (1931).
 REKVELD: Z. Physik **68**, 543 (1931).
 SAHA AND BHARGAVA: Nature **128**, 870 (1931).
 SCHAEFER, MATOSSI, AND ADERHOLD: Physik. Z. **31**, 801 (1930).
 SCHAEFER, MATOSSI, AND ADERHOLD: Z. Physik **65**, 319 (1930).
 SIRKAR: Indian J. Physics **5**, 663 (1930).
 SIRKAR: Indian J. Physics **8**, 67 (1933).
 UREY AND BRADLEY: Phys. Rev. **38**, 1969 (1931).
 WERTH: Phys. Rev. **36**, 1096 (1930).

III. Technique

- BARKER: Phys. Rev. **37**, 330 (1931).
 PAL AND SEN GUPTA: Indian J. Physics **5**, 609 (1930).

IV. Crystals

- BLACKMAN: *Naturwissenschaften* **21**, 367 (1933).
CZERNY: *Naturwissenschaften* **17**, 12 (1929).
HOLMES: *Phys. Rev.* **41**, 389 (1932).
REDLICH: *Z. Elektrochem.* **39**, 571 (1933).
SUTHERLAND: *Proc. Roy. Soc. London* **A141**, 535 (1933).

V. Water

- BOLLA: *Nature* **129**, 60 (1932).
BRUNETTI AND OLLANO: *Nuovo cimento* **7**, *Rivista* 223 (1930).
CARELLI AND WEST: *Z. Physik* **80**, 232 (1933).
ELLIS: *Nature* **123**, 205 (1929).
EMBIRIKOS: *Physik. Z.* **33**, 946 (1932).
GHOSH AND KAR: *J. Phys. Chem.* **35**, 1735 (1931).
GORDON: *J. Russ. Phys. Chem. Soc. (Phys. Pt.)* **61**, 353 (1929).
MEYER: *Physik. Z.* **32**, 293 (1931).
RAFALOWSKI: *Bull. intern. acad. polonaise* **1931A**, 623 (1932).
RAMASWAMY: *Nature* **127**, 558 (1931).
RAO: *Nature* **123**, 87 (1929).
RAO: *Nature* **132**, 480 (1933).
RASETTI: *Nuovo cimento* **8**, 191 (1931).
SUHRMANN AND BREYER: *Naturwissenschaften* **19**, 772 (1931).
VENKATESWARAN: *Z. physik. Chem.* **B1**, 466 (1928).

VI. Acids and bases

- BÄR: *Helv. Phys. Acta* **4**, 369 (1931).
MÉDARD: *Compt. rend.* **197**, 582 (1933).
RAO: *Nature* **124**, 762 (1929).
RAO: *Indian J. Physics* **8**, 123 (1933).
WOODWARD: *Nature* **126**, 58 (1930).

VII. Solutions

- BAUER, MAGAT, AND SILVEIRA: *Compt. rend.* **197**, 313 (1933).
DADIEU AND KOHLRAUSCH: *Sitzber. Akad. Wiss. Wien, Abt. Iib*, **139**, 459 (1930).
HANSEN-DAMASCHUN: *Z. physik. Chem.* **B22**, 97 (1933).
PETRIKALN AND HOCHBERG: *Z. physik. Chem.* **B3**, 217 (1929).
POHLMAN: *Z. Physik* **79**, 394 (1932).

VIII. Complex compounds

- PETRIKALN AND HOCHBERG: *Z. Physik* **59**, 114 (1929).

IX. Amorphous compounds

- WEILER: *Z. Physik* **81**, 424 (1933).

X. Liquids

- HEMPTINNE AND PEETERS: *Bull. sci. acad. roy. Belg.* **17**, 1107 (1931).
IMANISHI: *Bull. Inst. Phys. Chem. Research Tokyo* **16**, 1 (1931).

- PIÉNKOWSKI: Acta Phys. Polonica **1**, 87 (1932).
SUTHERLAND: Nature **126**, 916 (1930).
VENKATESWARAN: Nature **128**, 870 (1931).

XII. Gases

- BAILEY AND CASSIE: Phys. Rev. **39**, 534 (1932).
BAILEY, CASSIE, AND ANGUS: Nature **126**, 59 (1930).
BHAGAVANTAM: Indian J. Physics **6**, 557 (1932).
CASSIE AND BAILEY: Z. Physik **79**, 35 (1932).
COBLENTZ: Phil. Mag. [7] **7**, 203 (1929).
DEODHAR: Z. Physik **57**, 570 (1929).
LANGSETH: Nature **128**, 225 (1931).
LEWIS: Phys. Rev. **41**, 389 (1932).
MAHANTI: Physik. Z. **32**, 108 (1931).
MARTIN AND BARKER: Phys. Rev. **41**, 291 (1932).
MCLENNAN, SMITH, AND WILHELM: Phil. Mag. **14**, 161 (1932).
PLACZEK AND TELLER: Z. Physik **81**, 209 (1933).
PLYLER AND BARKER: Phys. Rev. **38**, 1827 (1931).
RAMDAS: Indian J. Physics **3**, 131 (1928).
RASETTI: Z. Physik **66**, 646 (1930).
VENKATESACHAR: Nature **124**, 838 (1929).

Reviews

- ANDREWS: Ind. Eng. Chem. **23**, 1232 (1931).
ANDREWS: J. Chem. Education **8**, 1133 (1931).
BRUNI: Giorn. chim. ind. applicata **13**, 464 (1931).
CLARK: Chem. Rev. **11**, 231 (1932).
ELSEN: Chem. Weekblad **29**, 1 (1932).
ELSEN: Chem. Weekblad **29**, 298 (1932).
ELSEN: Chem. Weekblad **29**, 183 (1932).
FILIPPOVA: Uspekhi Khim. **1**, 744 (1932).
KOHLEAUSCH: Scientia **51**, 335 (1932).
PAUL: Rev. gen. sci. **44**, 233 (1933).
RAMAN: Indian J. Physics **6**, 263 (1931).
SCHAEFER AND MATOSI: Fortschr. Chem. Physik. physik. Chem. **20**, 323 (1930).
SMEKAL: Z. Elektrochem. **36**, 618 (1930).
SZABO: Természettud. Közölny Potfuzetei (sup.) **63**, 1 (1931).
TISELIUS: Tek. Tid. Uppl. C. Kemi **63**, 1 (1933).
UREY: Ind. Eng. Chem. **23**, 1241 (1931).
VELLUZ: J. pharm. chim. **14**, 385 (1931).
WEIGLE: Arch. sci. phys. nat. **14**, 82 (1932).
WEILER: Physik. Z. **33**, 489 (1932).