RAMAN SPECTRA OF SOME SPECIES IN AQUEOUS SOLUTION

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Water absorbs strongly in the infrared region and consequently is a very unfavourable solvent for the investigation of the vibrational spectra of solute species by the infrared absorption method.

For Raman spectroscopy, on the contrary, water is not only a possible solvent, but indeed one of the most favourable because of the simplicity and unobtrusive nature of its own Raman spectrum. The only feature of any considerable intensity is the remarkably broad O—H stretching band. Though this extends over several hundred wavenumbers, it is situated at so high a Raman frequency (around 3440 cm^{-1}) that it does not interfere at all with normal solute spectra. There are some other weak bands, notably at about 1640 cm^{-1} (deformation) and about 175 cm^{-1} (intermolecular); but their intensity is so low as to be practically negligible. Change of temperature and the presence of dissolved solutes, both of which affect the molecular structure of the liquid water, cause changes of the band shapes and intensities[1-3]; but in general it is fair to say that the solvent spectrum does not give rise to any serious difficulty in the investigation of the spectra of solute species.

As regards experimental precautions, it is important that samples should be as far as possible optically clear, and with aqueous solutions this often demands centrifuging or passage through fine glass filters. For quantitative intensity work it is essential to remove even small traces of coloured impurities capable of causing absorption in the region under investigation.

Water is an excellent solvent for electrolytes, and consequently the Raman method assumes importance for the study of ions in solutions. It is true that the weakness of the Raman effect restricts its application to fairly high concentrations; but it is therefore especially valuable, since it is precisely in the region of high concentrations that the interpretation of results obtained by other methods meets with relatively serious difficulties.

The most straightforward type of application is for the determination of the symmetry of ions derived from strong electrolytes, especially salts, where complete ionic dissociation may be assumed. By application of the rules of selection and polarization, different proposed symmetries lead to different Raman "patterns"; and so observation of the actual pattern can discriminate between the different proposed structures. An extremely simple example is provided by a piece of work carried out over 30 years ago[4]. This concerned the mercurous ion in solution, for which some evidence had been obtained by another method that it was not monatomic (Hg$^+$) but diatomic (Hg$_2{}^{++}$). If monatomic, it would of course have no vibrational spectrum; if diatomic, it should show just one Raman line. In fact an aqueous solution of mercurous

nitrate was found[4] to give (in addition to the known spectrum of the NO_3^- ion) one intense line at 169 cm^{-1}. Thus the diatomic structure of the mercurous ion was directly confirmed. Incidentally this was the first observation of the stretching frequency of a metal–metal bond.

Since that time very many ionic species have been detected and characterized in aqueous solution by means of their Raman spectra. As an example I should like to report very briefly some aspects of recent work on plane square complexes of Pt (II), carried out by Ware in my laboratory at Oxford. The simple $PtCl_4^{2-}$ ion was first investigated by Stammreich and Forneris[5], and its Raman spectrum was as predicted for a planar square configuration. Ware has investigated a number of ions of the type PtX_3L^-, where X is a halogen (either Cl or Br) and L is a molecular ligand. All these species, like $PtCl_4^{2-}$, are strongly coloured, and consequently their Raman spectra cannot be obtained with the customary blue (Hg, 4358 Å) excitation. In Ware's work they were excited by the yellow and red lines (5876 and 6678 Å) from a suitable helium lamp source.

We will confine ourselves to the cases where L is an ethylene molecule. There is no doubt about the structure of these ions. X-ray diffraction evidence[6] has shown that the arrangement is based upon a plane square and that the C—C direction of the ethylene molecule is perpendicular to the PtX_3 plane. The point group is therefore C_{2v}. The special interest of these species lies in the nature of the bonding between the Pt atom and the C_2H_4 molecule, about which there has been much speculation. It has been suggested[7] that two types of bonding (not mutually exclusive) may be involved: first, a three-centre σ-type formed by donation of π-electrons from the ethylene to an empty dsp^2 hybrid orbital of the platinum atom; and secondly, a π-type formed by donation from the filled d_{xz} orbital of the platinum to the empty π^* anti-bonding orbital of the ethylene. The second type of bonding (or both types together) would constitute a kind of PtC_2 ring structure.

Some solid-state infrared studies of $PtCl_3C_2H_4^-$ have been reported[8], but Ware has for the first time obtained the Raman spectra of this ion and also of $PtBr_3C_2H_4^-$ in aqueous solution and has been able to propose fairly complete vibrational assignments. Two points of interest may be mentioned. The first concerns modes in which the ethylene molecule moves relative to the platinum atom. A polarized Raman line (at 401 cm^{-1} for the chloro-ion and 393 for the bromo-analogue) is assignable without doubt to the symmetric Pt—(C_2) stretching mode, in which both carbon atoms move in phase. There will also be a mode in which the carbon atoms move out of phase, *i.e.*, one of them moves away from the platinum atom while the other approaches it. Now if the ethylene molecule were attached to the platinum atom merely by a σ-type bond, this motion might be thought to involve angle changes rather than bond stretching and its frequency might be considerably lower than that of the symmetric stretching mode referred to above. But if a ring-type bonding is present, then the motion in question is to be regarded as involving asymmetric ring stretching and its frequency is expected to be near to (and probably greater than) the symmetric stretching frequency. In fact the latter is accompanied in the spectra of both complexes by a depolarized Raman line of *higher* frequency (490 and 485 cm^{-1} res-

pectively), and there seems no doubt that this must be assigned as an asymmetric Pt—(C_2) stretching mode. The observation thus suggests a considerable proportion of π-bonding, utilizing d-electrons of the platinum atom.

The second point concerns the C—C stretching frequency. Here our Raman assignments (1515 cm^{-1} for the chloro-complex and 1518 for the bromo-analogue) are in agreement with infrared evidence, all possible confusion with CH_2 deformations having been removed by the observation[9] that the frequencies in question show no characteristic shift on deuteration. It is notable that these C—C stretching frequencies are only about 100 cm^{-1} lower than that of the free ethylene molecule, indicating that the bond between the carbon atoms remains essentially a double bond and that the participation of the π-electrons of the ethylene molecule in the bonding to platinum is not very extensive. A full account of these investigations will be published in due course.

We turn now to the quantitative study of ionic equilibrium by Raman intensity measurements. Consider for example the ionic dissociation of perchloric acid. The determination of the concentration of ClO_4^- ions (and hence the degree of dissociation) in a given aqueous solution is in principle very simple, if one assumes that the intensity of a characteristic Raman line (*e.g.*, the intense ν_1 line) of the ion is directly proportional to its concentration. All that has to be done is to measure the intensity per gram ion by using as reference standard a solution of some perchlorate for which dissociation may be taken as complete.

The Raman method is specially powerful because the lines of a particular species are comparatively sharp and so remain distinct and recognizable even in the presence of other species. Measurements can thus be carried out solely upon the individual species (*e.g.*, the ClO_4^- ion) upon which interest is centred. This represents an important advantage over all colligative methods, including proton nuclear magnetic resonance. In the latter, measurement is of the concentration-weighted average of the chemical shifts of the protons in their various chemical environments. For a solution of an acid it is assumed that the different types of proton are (*i*) those in the water molecules, (*ii*) those present as hydrogen ions, and (*iii*) those in the undissociated acid molecules. It is necessary to introduce shift parameters for each type, and to assume that they remain constant at all acid concentrations. This assumption appears doubtful because of changes in the structure of the water and in the degree of hydration of the hydrogen ion. Moreover, in some cases it has been found necessary[10], in order to determine the parameters, to invoke concentrations obtained from Raman intensities; thus in this respect the proton nuclear magnetic resonance method is a derivative one.

In the case of perchloric acid, degrees of dissociation over a range of acid concentrations had been determined by the proton n.m.r. method[10] before any serious investigation by the Raman method. The values obtained were surprisingly low. Quite recently two independent investigations based on Raman intensities have been carried out[11,12]. Despite appreciable differences at high acid concentrations they agree in showing that, as anticipated, the earlier proton n.m.r. results were seriously in error.

This is not to say that the Raman method does not have its own difficulties as regards interpretation of measured intensities. In fact it is found that the observed intensity per gram ion of a species such as nitrate ion (characterized by the ν_1 line) in solutions of metal nitrates is not a constant, but shows appreciable specific variations with salt concentration. The question of how to obtain a satisfactory standard for the determination of the concentration of the ion in (say) a solution of nitric acid has been the subject of a good deal of discussion, and no little confusion seems occasionally to have arisen. Workers have sometimes undertaken so-called refractive index corrections without fully appreciating the factors involved.

Let us introduce a hypothetical intensity $I_{corr.}$ which shall, by definition, be directly proportional to volume concentration. If $I_{obs.}$ is the actually observed value, then we may write:

$$I_{corr.} = I_{obs.} \times R$$

where R is a correction factor. As pointed out by Rea[13],[14] R may be written as the product of two factors $R_{opt.}$ and $R_{int.}$. The former takes account of purely geometrical–optical apparatus effects, namely, reflections and refractions affecting both the exciting and Raman-scattered light. For a given apparatus it is a universal function of the refractive index μ of the sample, applicable to all samples irrespective of their chemical nature. The other factor $R_{int.}$ takes account of the specific influences of the local environment of the scattering molecule or ion in modifying the effective electric field of the exciting light and in perturbing the scattering species and so modifying its intrinsic Raman-scattering power.

Rea[13] has shown how the variation of $R_{opt.}$ with refractive index can be determined once and for all for any Raman source, by comparison with a special source so designed that its $R_{opt.}$ can be calculated. He has also measured separately[13],[14] the variation of $R_{int.}$ for a number of organic molecules at known concentrations in various solvents.

As we are concerned with a standard for concentration determinations (e.g., of NO_3^- in aqueous nitric acid solutions), it is appropriate to consider the intensity, I_{molar}, per mole or gram ion, i.e., the actual intensity divided by the volume concentration in moles or gram ions per litre: $I_{molar} = I/c$. All concentration determinations will be concerned only with ratios of intensities, and so the values may be conveniently scaled so as to make I_{molar} tend to unity at zero concentration. Also the determinations will involve only ratios of correction factors, and so we may likewise adopt a scale on which both $R_{opt.}$ and $R_{int.}$ also tend to unity at zero concentration.

As the salt concentration (and hence the refractive index μ of the solution) is increased, the value of $I_{molar, obs}$ departs from unity because of the changes of both $R_{opt.}$ and $R_{int.}$. The effect of $R_{opt.}$ alone is to cause $I_{molar, obs.}$ to fall roughly linearly with increase of μ. Over the range $\mu = 1.34$ to 1.42 normally encountered for aqueous solutions of electrolytes, the fall is likely to be about 5 per cent. The effect of $R_{int.}$ alone, on the other hand, will be expected (in the light of Rea's results) to cause $I_{molar, obs}$ to rise with increasing concentration, possibly by as much as 20 per cent over the same range. Thus the two factors are opposed and tend to compensate for one another, so that the actually observed value of I_{molar} will remain more

nearly constant than if either $R_{opt.}$ or $R_{int.}$ had been separately operative. Of course, different systems will be subject to different $R_{int.}$ effects, and so different variations of $I_{molar, obs.}$ are to be expected.

This expectation is indeed realized in the experimental results of Vollmar[15] for the nitrate ion in aqueous solutions of various metal nitrates. The observed differences of I_{molar} at high values of μ are mostly within 5 per cent, but may be as high as 10 per cent. With modern photoelectric instruments the precision of intensity measurements is better than this, and so the question of correction is seen to have practical importance.

Our object is to determine the correct concentration $c_{corr.}$, which is given by:

$$c_{corr.} = \frac{I_{corr.}}{I_{molar, corr.}} = \frac{I_{obs.}}{(I_{molar, obs.})_{St.}} \times \frac{R_{opt.}}{(R_{opt.})_{St.}} \times \frac{R_{int.}}{(R_{int.})_{St.}}$$

in which the subscript St. denotes the standard used. Some workers have undertaken a correction for the $R_{opt.}$ ratio, e.g., by using the value of $I_{molar, obs.}$ measured for a standard having the same refractive index as the solution under investigation. This certainly eliminates geometrical–optical apparatus effects, but it leaves in the $R_{int.}$ ratio which (as we have seen) may represent an error of 5 or even 10 per cent. Indeed a more nearly correct result might have been obtained by paying no attention at all to refractive index, and merely using the value of I_{molar} observed for a standard having about the same actual intensity as that of the solution under investigation.

In principle it is always possible to correct completely for purely geometrical–optical apparatus effects by independently determining $R_{opt.}$ as a function of μ for the particular apparatus being used. The difficulties arise on account of the specific $R_{int.}$ factors. In the present state of our knowledge these cannot be satisfactorily calculated. Moreover they can only be measured experimentally for a species in solution when its true concentrations are known. The position is thus an unsatisfactory one in the study of ionic equilibria, where it is just the true concentrations that we desire to determine.

It appears that the most satisfactory choice of a standard in any particular case will be the one whose specific $R_{int.}$ factors cancels as nearly as possible with that of the solution being investigated. Since $R_{int.}$ for this solution cannot be calculated or measured, we have to consider what observable criteria can be invoked as an indication of its relative magnitude.

For the nitrate ion Vollmar[15] has presented evidence which suggests that specific effects are likely to be small in ammonium nitrate solutions, and has suggested that the effects for other nitrates be assessed by comparison with the ammonium salt. As a related concentration-dependent observable, he focuses attention especially upon the shifts of the maximum of the near ultraviolet absorption band of the NO_3^- ion. Such shifts are expected to influence the Raman intensity by modifying the resonance Raman effect. In fact the observed variations of $I_{molar, obs.}$ are qualitatively in the expected sense, but the agreement with theory leaves much to be desired and in certain cases hardly merits the description "semi-quantitative".

Another observable quantity, not mentioned by Vollmar, is the splitting of ν_3 (the asymmetric stretching frequency of the NO_3^- ion), which has been

attributed[16,17] to lowering of the symmetry by cation perturbation, presumably corresponding to some kind of ion-pair formation. The splitting becomes more clearly apparent in concentrated solutions, but its magnitude is practically independent of concentration for each individual nitrate. It seems reasonable to inquire whether this quantity can serve as a measure of the effect of specific interactions upon the Raman intensity per gram ion. In fact, when $I_{molar, obs}$. values for different salts (expressed as percentages of the values for ammonium nitrate at the same μ) are plotted against splitting of ν_3, a very much smoother relationship is found than when the same intensity data are plotted against u.v. band-shifts. Another observable quantity connected with specific environmental effects is the half-width of
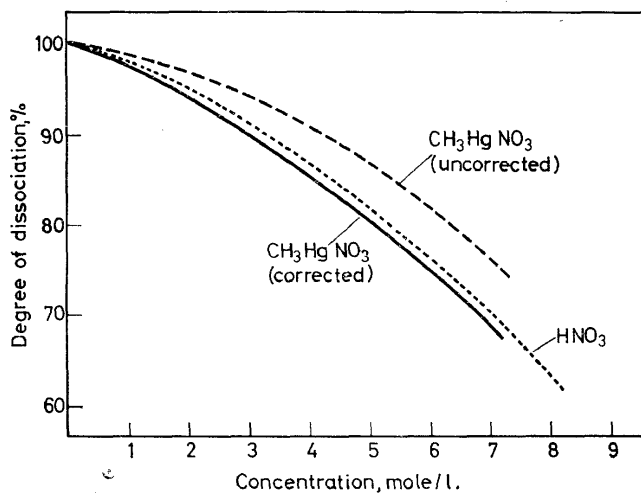

Figure 1. Dissociation of methyl mercuric nitrate in aqueous solution, determined by Raman intensity measurements

the ν_1 Raman line of the nitrate ion. Here again a fairly satisfactory relation to observed molar intensity is found. These admittedly empirical findings assume practical importance in choosing a standard for concentration determinations by the Raman intensity method. The most satisfactory choice, *i.e.*, the one most likely to cause the desired cancellation of specific R_{int}. factors, will clearly be the salt solution which shows as nearly as possible the same splitting of ν_3 and the same broadening of ν_1 as are observed in the solution being studied.

I should like to conclude with a brief advance account of measurements on aqueous solutions of methyl mercuric nitrate at approximately 0°C at present being carried out by Clarke in my laboratory in Oxford. In 1962 Goggin and Woodward[18] found that the Raman spectrum of a concentrated solution of this compound in water consisted of a superposition of spectra attributable to the NO_3^- ion, the hydrated CH_3Hg^+ cation and the undissociated CH_3HgNO_3 molecule. The system is thus closely analogous to that of nitric acid in aqueous solution. We have now determined the degree of dissociation of CH_3HgNO_3 as a function of concentration by means of

Raman intensity measurements upon the ν_1 line of the NO_3^- ion, the principle being exactly the same as for nitric acid.

Despite the equilibrium involving undissociated molecules, the "free" NO_3^- ions in aqueous solutions of methyl mercuric nitrate appear to suffer only small specific perturbation, as judged by the half-width of the ν_1 line. Since specific effects are also believed to be small in ammonium nitrate solutions, we have considered it best to choose this salt as standard and to determine concentrations of "free" nitrate ions (and hence degrees of dissociation α) from the ratio of the observed intensity to the value of $I_{molar, obs.}$ for an ammonium nitrate solution of the same refractive index. (In practice, owing to the relatively high μ-values of CH_3HgNO_3 solutions, some extrapolation of the experimental results for NH_4NO_3 was necessary.)

The full line of *Figure 1* shows the percentage dissociation (thus determined) as a function of total CH_3HgNO_3 concentration. The broken line shows the corresponding result, using values of I_{molar} at the same $I_{obs.}$ rather than at the same μ, as the solutions under investigation.

Also included is the corresponding curve (dotted) for nitric acid at 25°C, as given by Young, Maranville and Smith[19]. These authors state that a "correction for refractive index" has been applied, but do not explain its nature. Moreover, their choice of $NaNO_3$ solutions as standards does not seem to have been a good one, in view of the fact that the broadenings of ν_1 (and hence probably the specific intensity effects) appear to be considerably different for HNO_3 solutions, as compared with $NaNO_3$ solutions. The exact significance of a comparison of the curves for CH_3NO_3 and HNO_3 is therefore not clear; but at least Clarke's results show that methyl mercuric nitrate is an electrolyte which is dissociated to approximately the same extent as nitric acid. This is an interesting illustration of the apparent similarity between the CH_3Hg^+ ion and the H^+ ion, other aspects of which are also being investigated. A complete account of this work will be published in due course.

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