

LONG-WAVE EXCITATION OF RAMAN SPECTRA

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Six years ago, at the Oxford meeting of this group, I had the privilege of reporting on the technique and results of excitation of Raman spectra in the red and near infra-red region¹. On this occasion, I shall try to give a brief account on some improvements that have been made to the method since then, and to relate some typical examples of applications.

It has been said that the discovery of the Raman effect, and certainly its wide application to molecular spectroscopic studies, are largely due to the mercury lamp. Indeed, the almost exclusive features of the mercury spectrum and the facility with which powerful lamps can be constructed in nearly any desired geometrical form make this light-source particularly suitable for the excitation of Raman spectra. The advantages of using the enclosed mercury arc for such work are so obvious that one tends, perhaps, to overlook its inconveniences. In particular, the best use has not always been made of the inherent property of the Raman spectrum not to be confined to a given spectral region but to have a position which is determined by the wavelength of the exciting radiation.

A further reason for the predominant use of the ultra-violet, violet and blue mercury lines for excitation is to be seen in the fact that, during the first fifteen or twenty years of Raman spectroscopic work, nearly all studies had to be carried out by means of prism spectrographs. The low intensity of the Raman scattering and, therefore, the necessity of combining high light gathering power with sufficient dispersion has led to the use of the short-wave region of the prismatic spectrum. The ever-increasing application of infra-red spectroscopy in recent decades has been made possible by the development of a great variety of instruments suited to the spectral range, resolution, *etc.*, required by the specific problem. The same trend has not prevailed in Raman spectroscopy, since the particularities of such work have seldom led to commercial constructions of highly specific instruments. Usually, slightly modified spectrographs intended for general investigations of weak luminous phenomena have to be employed. In many instances Raman studies have been carried out, and are carried out, by means of devices constructed in the laboratory of the investigator.

The excitation of Raman spectra of coloured, fluorescent or photosensitive compounds by mercury radiations is almost impossible. It is, perhaps, by the very nature of progress in chemistry that some large groups of newly-discovered compounds, presenting interesting problems of structure and bond properties, cannot be investigated by means of the conventional Raman techniques. As examples, organometallic co-ordination compounds such as "sandwich molecules", metal carbonyls and their derivatives can be mentioned. Frequently, the weak linkages in such complexes and the large masses of the atoms or ligand groups involved give rise to low-frequency vibrations which are difficult to observe in infra-red absorption. Also, the

fact that highly symmetric molecular configurations usually possess more Raman-active normal modes than infra-red-active ones might be taken into consideration. This holds true particularly for the tetrahedral and octahedral structures, and also frequently for point groups D with three-, four-, five- or six-fold symmetry axes.

The foregoing considerations suggest the desirability and the potentialities of exciting Raman spectra in the long-wave region. Ten or fifteen years ago it seemed hardly possible to envisage a practical and promising experimental technique for the recording of Raman spectra in the red or near infra-red region. The sensitivity of available radiation detectors, whether photographic plates or photomultipliers, was much too low at long wavelengths. Since then, considerable improvements have been made in increasing the sensitivity of photographic emulsions in the far red and near infra-red, and, more recently, photomultiplier cells which possess the characteristics required for Raman work in this spectral range have been developed. The rapidly decreasing dispersion of the prism with greater wavelengths and the low efficiency of non-blazed gratings discouraged, in the past, the construction of a Raman spectrograph suitable for long-wave excitation. The latter disadvantage has been removed by the marked progress that has been made in the manufacture of blazed gratings with high efficiency, comparing favourably with prism instruments. Another difficulty, at present only incompletely overcome, is that of obtaining adequate light-sources providing, at least in part, the facilities of the mercury arc used in the conventional Raman work.

Yet the most serious obstacle for routine work in the long-wave region is, apparently, the fourth-power law which operates in the phenomena of light-scattering. The intensity of the Raman spectrum, already weak when excited in the usual way, decreases with the fourth power of the wavelength. However, it can be shown that this additional loss may be fully counterbalanced by the use of a grating spectrograph and by taking advantage of the principles of photographic recording. This is due to the fact that the diffraction angle of the grating is a nearly linear function of the wavelength, while the pertinent parameter for spectroscopic studies is, usually, the dispersion by frequency or wave-number. The wavelength \times wavenumber product is a constant, and hence a grating spectrum, having approximately a constant dispersion by wavelength, shows a dispersion in the frequency scale which increases with the square of the wavelength. Consequently, the ratio of wavelength to wavenumber rapidly becomes more favourable towards the red and near infra-red region. A wavenumber difference of 10 cm^{-1} in the spectral region of the conventional Raman work, *i.e.* at 4000 or 5000 \AA , corresponds to wavelength intervals of 1.6 and 2.5 \AA respectively; at 8000 and 10000 \AA , the same lines are separated by 6.4 and 10 \AA respectively. In order to attain a required dispersion in the frequency scale, we may thus photograph the grating spectrum by means of cameras of focal lengths which decrease with the square of the wavelength and increase the angular aperture of the camera lens in the same proportion. On the other side, it is well known that the photographic speed of a spectrograph provided with a dispersing system, prism or grating, of given dimensions does not depend upon the focal distance of the collimating lens, but is determined exclusively

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by the angular aperture of the camera lens. The photographic speed increases with the square of the magnitude of the latter quantity. Consequently, for Raman work in the long-wave region, we usually employ unsymmetrical spectrographs by reducing the focal length of the camera lens in proportion to the square of the wavelength of the exciting radiation while keeping its diameter unaltered. In this way, it becomes feasible to set up very small and inexpensive instruments providing, as compared with those used in the conventional technique, spectra of identical dispersion over the frequency scale and having a photographic speed which increases with the fourth power of the wavelength. That means that the decrease in intensity according to the fourth-power law can be entirely compensated when the spectrum is recorded photographically. In some instances, we use extremely rapid camera lenses, of reciprocal angular apertures down to 0.7, which have recently become available for the photography of rapidly moving images on the fluorescent X-ray screen. Conversely, using a conventional spectrograph of medium light-power and medium dispersion, one may attain high dispersions and high resolution in the long-wave region; some examples of such applications will be given later.

A further characteristic feature which is inherent to the methods of long-wave excitation may be mentioned. Raman spectra of coloured compounds are usually excited by the shortest wavelength possible, *i.e.* the exciting frequency is close to that of an electronic absorption band of the molecule. This leads to an appreciable decrease in the value of the resonance denominator and, consequently, to a gain in intensity of the Raman scattering. Even without attaining the boundary line of the resonance Raman effect in the narrower sense of that term, we frequently observe surprisingly strong Raman spectra.

An additional advantage of the above-mentioned unsymmetrical spectrographs, provided with camera optics of short focal length, is the use of comparatively large slits. Normally, the practical limit of resolution of a Raman spectrograph is not determined by the intrinsic resolving power of the dispersing device, but by the coarse grain of the sensitive photographic plates which have to be employed and which limits the effective resolution to 40 or 50 lines/mm. Hence, it would be unprofitable to produce an image of the slit narrower than is compatible with the resolving power of the plate, and the cameras of high angular aperture may be used in combination with wide-entrance slits.

As the source of excitation in the 6000–8000 Å region, we continue to make use of helium discharge tubes of the cold cathode type which are wound helicoidally around the Raman tube. For short cells, as used for liquid samples, the potential drop in such lamps is of the order of 2,000 V and the current is about 0.5 amp. It should not be difficult to triple the light output of such lamps by providing them with hot cathodes and employing currents of approximately 2 amp. Promising results may also be expected from the use of electrodeless microwave-powered discharge tubes whose application to Raman work has been proposed and tested by Ham and Walsh². In the near infra-red region, we successfully excited the Raman spectra of some diatomic molecules by radiations of other inert gases such as argon, krypton and xenon, but the use of the resonance doublets of alkali

metals appears to be particularly promising in this region. During the war, powerful caesium lamps were developed for infra-red communication purposes, and such sources could readily be adapted to Raman work. Profitable use has been made even of small lamps of this kind; they are at present the only ones which are commercially manufactured. Miller *et al.*³ excited the Raman spectrum of chromyl chloride with the resonance lines of potassium; recently we have often employed rubidium vapour lamps by mounting six small units in a light furnace. Each of them consumes only 10 watts and has a discharge column 15 mm long. This light-source enabled us to record the Raman spectra of some halogens, interhalogens and polyhalide ions in solutions that were completely opaque to visible light.

Raman studies on small crystals and of turbid solutions require the use of secondary filters possessing narrow absorption bands, in order to remove excess stray light of the wavelength of the exciting radiation without seriously affecting the intensity of Raman shifts close to the exciting line. In conventional Raman spectroscopy, satisfactory spectra may often be unobtainable owing to the lack of efficient filters possessing the required properties; in this respect the conditions in the long-wave region are more favourable. In particular, liquid filters containing ions of the rare earth elements have proved to be useful, thanks to the narrowness of the absorption bands which, in some instances, are nearly line-like. An aqueous solution of erbium perchlorate allows for the almost complete removal of the helium line at 6678.2 \AA without any appreciable weakening of Raman bands of frequencies as low as 40 cm^{-1} . In a similar way, praseodymium salts may be used to absorb the yellow helium line at 5875.6 \AA . Solutions of neodymium salts absorb the 7947.6 \AA component of the rubidium resonance doublet, without affecting the intensity of the other component at 7800.2 \AA which has twice the intensity of the other line.

In order to re-absorb the resonance radiations of the alkali-metal vapour lamps, employed for the excitation of Raman spectra, one might take advantage of the absorption of the same metals in the gaseous state. Just as the classic Raman studies of Rasetti on the pure rotational spectra of nitrogen and oxygen were made possible by the use of mercury vapour absorbing the exciting resonance mercury line at 2536 \AA , one may use potassium, rubidium or caesium vapour as secondary filters for the respective resonance radiations.

Now we shall briefly examine the possibilities of photo-electric recording of Raman spectra in the long-wave region. Whereas the photographic speed of a spectrograph depends upon the quantity of light falling on the unit area of the plate, it is the total intensity of the radiant "bundle", transmitted by the instrument, that provides the response of the photo-cell. Of course, the amount of radiant energy cannot be increased by altering the aperture of the image-forming optical system. Hence, this advantage, so decisive in photographic recording, vanishes, and the decrease of intensity according to the fourth-power law has to be taken into account. Nevertheless, Raman spectra excited by the yellow helium line at 5875.6 \AA have been registered successfully by Pivavrov *et al.*⁴ up to vibrational frequency shifts of the order of 1600 cm^{-1} . Recent improvements in multiplying cells, combining high sensitivity to red and near infra-red radiations with a low noise level,

point to their prospective application in the long-wave Raman technique. Such multipliers have been developed especially for scintillation counting⁵, where extremely low anode dark-currents and noise are indispensable. Further improvements along this line might lead to the use of the very intense helium radiation at 10,830.3 Å for the excitation of Raman spectra, thus opening a new field of investigations farther into the infra-red region. For the time being, it seems premature to discuss in any details the possibility of applying lasers in such work.

Finally, we shall give a very brief account of some Raman studies, recently carried out in our laboratory, which may be considered as typical applications of the above-mentioned methods.

Carbon tetrachloride is extremely sensitive to light and to oxidative decomposition, particularly in solution. In the solid state, the compound is a little more stable, but even freshly prepared crystals are rather turbid and their surface soon becomes covered with iodine. By means of the erbium perchlorate filter already described, we succeeded in recording the Raman spectrum of the molecule in solution and in the solid state, excited by the helium line at 6678.2 Å⁶.

Potassium octacyanomolybdate, containing the ion $\text{Mo}(\text{CN})_8^{4-}$, is one of the comparatively rare compounds involving the co-ordination number eight. Only very few representatives of molecules possessing eight identical ligands are known. The state of hybridization of the central atom and the possible molecular structures resulting therefrom have been widely discussed. Aqueous solutions of the above compound are not strongly coloured, but decompose and become turbid upon the incidence of light of short wavelength. Making use of the erbium perchlorate filter, we excited the Raman spectrum of the ion by the helium line at 6678.2 Å. The observed spectrum points strongly to the square Archimedean anti-prism structure belonging to the point group D_{4d} . This result is in disagreement with previous X-ray diffraction measurements, which support the lower D_{2d} symmetry corresponding to a dodecahedral arrangement. Hitherto the latter configuration has been generally accepted, but it seems hardly compatible with the chemical properties of the compound⁷.

Dibenzene chromium and its cation are strongly coloured, as are nearly all aromatic complexes of the transition metals, commonly termed "sandwich molecules". The pentadienyl compounds of this kind, e.g. ferrocene, are rather stable and measurement of their Raman spectra in the long-wave region offers no particular difficulty. The contrary holds for dibenzene chromium and its iodide, owing to their pronounced sensitivity to light and oxygen. Further complications arise from the fluorescence of both compounds in solution. However, the complete Raman spectrum of the iodide and a partial one of the neutral molecule have been obtained by long-wave excitation⁸.

Metal carbonyls and their derivatives offer a large field for Raman spectroscopic studies by means of the methods outlined. The Raman spectrum of iron pentacarbonyl⁹, red-coloured and photosensitive, has confirmed the trigonal bipyramidal structure of the molecule belonging to the point group D_{3h} and has made it possible to calculate the significant force constants¹⁰ through a normal co-ordinate analysis.

Aqueous solutions of the sodium salts of cobalt and of iron carbonyl hydride are colourless, but are decomposed almost instantaneously by traces of oxygen or by radiations of wavelengths below 5500 Å. The complete Raman spectra of the tetrahedral ions $\text{Co}(\text{CO})_4^-$ and $\text{Fe}(\text{CO})_4^{2-}$, both iso-electronic with nickel carbonyl, were recorded by long-wave excitation¹¹. The force constants, calculated from the observed Raman frequencies, seem to provide significant information concerning the nature of the chemical bonding in the three species mentioned^{11,14}.

Especially interesting is the problem of the structure and linkage of the binuclear heavy-metal derivatives of cobalt carbonyl hydride, such as $\text{Hg}(\text{Co}(\text{CO})_4)_2$ and $\text{Cd}(\text{Co}(\text{CO})_4)_2$. Solutions of the former compound are the most photosensitive Raman samples we have ever dealt with; the cadmium derivative is chemically less stable than the mercury compound, but its decomposition by light is less pronounced. The Raman spectra of both molecules, excited by helium radiations, point strongly to the highly symmetric D_{3d} configuration and to the linkage of the heavy-metal atom to the cobalt carbonyl groups through a metal-metal bond¹⁴.

Iodine, iodine monochloride and iodine monobromide, when dissolved in organic solvents, are practically opaque to visible radiations, at least at the concentrations which are required for the study of their Raman spectra. The same holds true for solutions of the polyhalide ions I_3^- , IBr_2^- and others. The Raman spectra of these species have been recorded in the 8000 Å region, using the resonance lines of rubidium for excitation. In this way, information on solute-solvent interactions has been obtained which points, in some instances, to the formation of loose charge-transfer complexes or to stronger solute-solvent complexes.

High resolution Raman spectra in the long-wave region may be recorded, as pointed out above, by means of grating instruments which would provide in the conventional range only spectra of medium dispersion and resolution. This is due to the fact that the dispersion by frequency increases with the square of the wavelength. The methods of high-resolution Raman spectroscopy in the blue region of the spectrum have been greatly improved in recent years thanks, particularly, to the work of Welsh¹² and Stoicheff¹³ on pure rotational and on rotation-vibration Raman spectra. In order to attain effective resolutions varying between 0.5 and 2.0 cm^{-1} necessary for such work, these authors^{12,13} had to use a rather complicated and expensive apparatus which required delicate adjustment. Inexpensive instruments, which appear almost pocket-sized in comparison with the spectrographs used by the Canadian workers, are capable of providing a practical resolution of the same order or better in the near infra-red and even in the 6000 Å region. Especially valuable for this purpose are the small plane reflectance gratings having 2,160 grooves/mm; they are available with first-order blaze at 6000 Å^{15,16}.

By setting up such a grating with a 30 cm collimator and by using camera lenses of focal length 18 or 24 cm with angular apertures 1 : 2.8 and 1 : 4 respectively, we recorded the Raman spectrum of natural liquid chlorine, excited by the yellow helium line at 5875.6 Å. Not only were the fundamental shifts belonging to the three isotopic species $^{35}\text{Cl}_2$, $^{35}\text{Cl}^{37}\text{Cl}$ and $^{37}\text{Cl}_2$, present in the relative abundances 9 : 6 : 1, easily resolved, but equally

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well the respective upper stage bands which correspond to the transitions between the first and second excited vibrational levels. The intensity of the latter bands relative to the fundamental shifts is determined by the Boltzmann factor, which is, in the present case, approximately $\frac{1}{12}$. Hence, the intensity of the first upper stage band of species $^{37}\text{Cl}_2$ is about one-hundredth of that of the fundamental of $^{35}\text{Cl}_2$; even this weak Raman line could be recorded with comparatively short exposures.

The observed frequency-differences between fundamental and upper stage bands have led to the direct determination of the first-order anharmonicity constant of the chlorine molecule. The hitherto accepted value, obtained by the analysis of the band spectrum, is apparently 60 per cent too high¹⁵.

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