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New Possibilities and Chemical Applications of Raman Spectroscopy

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The problems involved in the study and applications of Raman spectroscopy are considered, attention being mainly concentrated on resonance Raman spectroscopy. Theoretical studies are briefly surveyed and the applications of the method in the investigation of molecular structures and the mechanisms and kinetics of chemical reactions are discussed. Examples of the study of various organic, organometallic, and other compounds, polymers, haemoproteins, nucleotides, etc. are presented. The possible applications of the excitation spectra of resonance Raman lines are noted.
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I. INTRODUCTION

Raman spectroscopy is widely used in chemistry, physics, and other branches of science as one of the most important methods for the investigation of molecular structure. The set of characteristic vibration frequencies determined from the spectra together with intensity data for Raman lines yield information about the force constants of chemical bonds, molecular symmetry, the presence of definite structural groups in the molecule, and the interaction of these groups with one another. Raman spectroscopy makes it possible to determine the compositions of fairly complex products and helps to determine the structures of new compounds and to elucidate the mechanisms of chemical reactions [1-8].

However, in the first stages of the development of the method, its scope was limited to fairly severe conditions. Practical experience showed that the Raman effect may be excited by monochromatic light of any wavelength, provided that it lies in the range where the test substance is completely transparent (i.e. is remote from absorption bands). The substance scatters only a small proportion of the incident light (less than one thousandth under laboratory conditions); furthermore, almost the entire scattering

is of the undisplaced (Rayleigh) type, while Raman scattering, which carries the most interesting information about molecular properties, constitutes only a few per cent of the total. Bearing in mind that less than one ten thousandth of the light scattered in all directions can be directed to the measuring apparatus (spectrometer), it is easy to imagine how small are the measured light fluxes of the individual Raman lines. In practice they can be observed only for high concentrations of the substance ($> 1\%$).

In attempts to excite the Raman effect in coloured substances in the region of absorption bands, virtually complete reabsorption occurred and the Raman lines were lost. It was suggested that under these conditions Raman scattering must be converted into fluorescence. Further theoretical studies showed that the transition to fluorescence is possible, but only in specific instances. On excitation by narrow spectral lines in the region of a fairly broad absorption band, typical Raman scattering should occur and be characterised by very high molar intensity coefficients[9].

In order to observe this effect, it was necessary to modify somewhat the usual experimental conditions; thereby it was possible to obtain distinct spectra of intensely coloured compounds. Thus, as early as 1948,[10] the Raman spectra of *p*-nitroaniline solutions were obtained with excitation in the violet part of the spectrum (within the half-width of the very intense band associated with the $\pi \rightarrow \pi^*$ electronic transition). Later the spectra of potassium *p*-nitrophenoxide were obtained with excitation at the absorption band maximum[11]. The intensity coefficients of the Raman lines were so high that the spectra were obtained without difficulty at concentrations $< 0.001\%$. The phenomenon described was called the resonance Raman effect[12].

Further studies demonstrated the possibility of observing the resonance Raman effect in chemical compounds of different classes[1]. Many objects, which previously could not be investigated by Raman spectroscopy, began to be studied with a fair degree of success. Measurements of the spectra of coloured liquid, gaseous[13-16], and solid substances were described, namely amorphous[17,18] and crystalline (semiconductors[19-24], non-conductors, various polymers[25,26], and minerals[27]) substances, monomolecular layers[28,29], chemical reaction intermediates present in solutions, free radicals[30-34], impurity centres in crystals[35-43], molecules in solid matrices[44-48], molecules in an electronically excited state[49], and compounds in natural systems (in the living tissues of plants and animals)[50-52]. One may note successful attempts at selective investigation of the structures of particular fragments of very complex molecules in whole erythrocytes[53], in the retina of a functioning eye[54], in bacteria[55,56], in viruses[57], etc. The spectra of a number of metals and metal compounds[58,59], wood charcoal, carbon black, etc. have been obtained[60]. The study of the resonance Raman effect promoted the solution of important problems of the interaction between light and matter and the elucidation of relations between principal molecular-optical phenomena[1,9].

The development of resonance Raman spectroscopy led to the establishment of an extensive branch of science within the limits of which new research fields began to be initiated; outwardly this was reflected by the appearance in Journals of new terms: "resonance Raman photochemistry",[61] "resonance Raman spectro-electrochemistry",[62-64] "internal reflection resonance Raman spectroscopy",[65] "X-ray resonance Raman spectroscopy",[66] etc.

Hitherto we spoke mainly of light scattering by molecules accompanied by excitation of molecular vibrations. The experimental observation of resonance rotational[67-69] and electronic[70] Raman light scattering by molecules, the electronic resonance Raman effect excited by X-rays in atoms[66,71,72], resonance scattering with spin-flip[4,73] and with excitation of magnons (spin waves)[74,75], excitons, and phonons (collective atomic vibrations in the crystal lattice)[76-83], and resonance-stimulated[84-87], inverse[88-90], and coherent[91-94] Raman scattering has been described in the literature in recent years. A sharp increase of the probability of Raman scattering and an increased applicability of the relevant methods to the study of molecules, crystals, and natural and technical products was noted in all cases.

Considerable progress in the experimental technique greatly extended the range of problems susceptible to solution by Raman spectroscopy. For example, the measurement of the spectra of atoms at the instant of collision in the gas phase, of individual optically active components of racemates, of flames, and of streams of exhaust gases from a reactive engine, accurate determination of the moments of inertia of molecules with revision of interatomic distances, and the study of the vibrational energy distribution of molecules formed in chemical reactions, of the distribution of electron densities in different parts of a single crystal, of the orientation of molecules in polymer blocks, etc. have become possible.

Delhaye[5] (Schmid, pp. 747 and 762) reported successful experiments involving the measurement of the Raman effect within 10^{-10} s, which gives rise to interesting prospects for the investigation of unstable species and the kinetics of rapid reactions (we may recall that at one time exposures lasting several minutes were regarded as a major achievement). A method has been developed for obtaining the images of microscopic objects at wavelengths of specified Raman lines ("micro-Ramanography"), which makes it possible to characterise the distribution of particular inclusions in homogeneous objects and to follow the chemical reactions in the latter.

Apparatus for measurements at a distance and for the investigation of remote objects under laboratory and field conditions (for the determination of flame temperatures, of the contamination of the atmosphere and water in the ocean, etc.) has been described. Ways of employing the method in astrophysics have been outlined and the parameters of Raman spectra have been used in the study of the atmosphere and in the determination of the geometrical albedos and diameters of planets on the basis of a determination of the rotational-vibrational satellites of Fraunhofer absorption lines arising in the scattering of the sun's rays by the planet's atmosphere[95-97].

The use of resonance excitation of the Raman effect has potential for a considerable improvement of the sensitivity and selectivity of the methods enumerated above.

As a result of the improvement of the experimental technique, many difficulties in the observation of the resonance Raman effect (for example, interference due to fluorescence) can be eliminated or reduced. Apparatus employing ultraviolet radiation has greatly extended the range of chemical compounds susceptible to resonance excitation. Thus nucleotides[98,99], simple amines, amides, dienes[100-103], benzene[104], etc. were investigated. Sources of monochromatic radiation with a smoothly adjustable frequency have created a considerable scope for the measurement of the excitation spectra of Raman lines, i.e. curves defining the dependence of Raman line intensities on the frequency of the exciting light $I(\nu)$. The study

of excitation spectra, which may be regarded as a new and important branch of resonance Raman spectroscopy, has given rise to considerable possibilities for the investigation of molecules not only in the ground state but also in excited electronic states [9,105,106].

Below we shall briefly consider the main lines in the development of the theory of the resonance Raman effect and the chemical applications of the method. Problems closely related to those considered here have been considered in the past few years in certain specialised reviews (problems of conjugation [1], problems of the theory of the resonance Raman spectroscopy of molecules [9,107,108] and crystals [109,110], experimental investigations and technique [111], and the applications of the resonance Raman effect in biochemistry [112,113]).

II. ADVANCES IN EXPERIMENTAL TECHNIQUE

During the initial period of the study of excitation spectra, it appeared appropriate to employ three–four wavelengths in order to characterise $I(\nu)$ approximately in the region of broad absorption bands in the visible part of the spectrum. The development of tunable lasers made it possible to cover the range 3000–7000 Å with any required number of points and to obtain information about the $I(\nu)$ relation, including the regions of the fine structure of the absorption spectrum, where a series of extrema were recorded with intervals smaller than 1 cm^{-1} for varying excitation frequency ν. [114] Indirect methods for characterising the excitation spectra (employing the change in the positions of absorption bands with variation of the composition of binary systems [76,116], the solvent [115,116], the temperature of the substance [17,77], the pressure, etc. at a fixed frequency ν) have now become of secondary importance.

The use of very short exciting light pulses (10^{-11}–10^{-8} s) and the recording of secondary resonance radiation with time scanning and separate observation of synchronous glow and afterglow are of exceptional interest. The pulse technique has been used, on the one hand, to study the mechanisms of the resonance transformation of light by molecules [117] and, on the other, to investigate short-lived intermediates by the resonance Raman method [118].

Excitation in the region of absorption bands may give rise to considerable experimental difficulties from the large light losses in the specimen and the photochemical decomposition of the substance. The light losses are reduced to a minimum by optimising the concentration of solutions (this was used already in the first observations of the resonance Raman effect [11] and has been specified in detail [119,120]) or by reducing the optical path length in the absorbing medium with selection of light scattered by surface layers of the specimen in the direction opposite to that of the incident light [121]. In another version the light beam is directed through a transparent plate or layer of liquid at a low angle onto the interface with a coloured solution [27,122]; the reflected light is enriched in the spectral components of the light involved in resonance Raman scattering as a result of the interaction of the incident light with the molecules in the surface layer of the coloured substance. The distribution of surfactants in a monomolecular layer at the interface with respect to molecular orientations was characterised by a similar method [28].

The interference due to the photochemical decomposition of the substance is reduced by scanning the incident light beam over the surface of the specimen [123], by rapid rotation of the cuvette [111], or by employing a flow technique [124–127]. For a flow rate of 1–10 m s^{-1}, which is readily attainable, it is possible to obtain distinct resonance Raman spectra of relatively unstable products [128]. The kinetics of the rapid reaction between horseradish peroxidase and hydrogen peroxide have been studied in this way [129]; the resonance Raman spectra were recorded a fraction of a second after mixing the reactants and the start of the reaction and at long time intervals; by selecting a particular zone along the length of the stream it was possible to detect the formation of unstable intermediates and to characterise the kinetics of their decomposition.

The interference due to fluorescence may be eliminated by employing a series of procedures: 1. By adding quenching agents (for example, nitrobenzene) [130,131]. 2. By modulating the polarisation of the incident radiation [132] and separating the polarised Raman lines from the depolarised fluorescence. 3. By modulating the frequency of the measured secondary radiation and recording the derivative $dI/d\omega$, whereby one can isolate resonance Raman lines which are narrower than the fluorescence lines; it is more effective [133] to modulate the frequency of the incident light, so that the positions of the fluorescence bands are not modulated, (in contrast to those of the Raman lines) and the receiving device does not record them [134]. 4. By illumination with short pulses combined with synchronous recording of the secondary radiation but not the afterglow [111,135]. 5. By carrying out measurements in the anti-Stokes region (see Section IV). 6. By ensuring the maximum monochromatisation of the incident light.

III. THE RESONANCE RAMAN EFFECT WITH EXCITATION OF ATOMIC VIBRATIONS

The resonance Raman light scattering by molecules, which takes place with excitation of atomic vibrations, has been most thoroughly investigated and has found extensive applications in chemistry and physics. The resonance conditions arise when the frequency of the incident light ν is in the region of the absorption band of the substance corresponding to the $0 \rightarrow e$ electronic transition. Such bands are usually located in the visible or ultraviolet regions; for many compounds in the vapour phase they have a fine vibrational-rotational structure but are very broad for solutions (500–5000 cm^{-1}). On irradiation with quasi-monochromatic light, the secondary radiation includes that produced by the resonance Raman effect in the form of narrow lines and possibly (cf. Ref. 136) fluorescence bands, which are usually just as broad as the absorption bands [137,138]. In those cases where the fluorescence spectrum consists of narrow lines, the latter may be mixed with the Raman lines [45,139–145], hindering the interpretation of the spectrum; the broad fluorescence bands interfere with the recording of the Raman scattering.

Resonance excitation does not modify the observed vibrational frequencies ω and the contours of the Raman lines, but increases the line intensities by several orders of magnitude [9–11,144,145]. On the other hand, the quantum yield of the Raman scattering [146] changes only slightly and remains very low [126,147–150]; for aromatic nitro-compounds in solution, it amounts to about 10^{-8} and depends comparatively little on the properties of the solvent and temperature (this cannot be said of fluorescence) [137,138].

Table 1 presents as an example the parameters [137] of the usual fluorescence (including the afterglow time τ_e) and the lines due to the nitro-group in the resonance Raman spectrum of 4-dimethylamino-4′-nitrostilbene after excitation with light in the region of the maximum of the $\pi \rightarrow \pi^*$

broad absorption band (~ 23 000 cm^{-1}); I^S is the molar intensity coefficient of the Raman line[1].

In successive experiments with excitation using light corresponding to different $0 \rightarrow e$ bands of the same substance, it is possible to observe resonance-induced intensification of various sets of Raman lines[79-81,151-154], preferentially those corresponding to fully symmetrical vibrations. The similarity between the locations (and orientations) of the electronic and Raman transitions is then important[128,155,156,184]. For example an intensification of the Raman lines due to the Co–N bond in the $Co(NCS)_4^{2-}$ ions was noted when the frequency ν was in the range corresponding to the band associated with the electronic excitation of Co–N bonds and an intensification of the C–N and C–S lines was observed on excitation of the Raman effect in the region corresponding to the short-wavelength absorption band due to the electronic excitation of the ligands[157]. Ultimately, everything depends on the electronic transitions which are influenced by particular atomic vibrational modes (see Section V). The electronic transitions which make a significant contribution to the intensity of a Raman line are said to be "effective" for this line[144,158]. However, this term was subsequently frequently used with another significance--implying a "centre of gravity" of the contributions of different transitions (this interpretation is permissible for Rayleigh scattering but hardly for Raman scattering, where the contributions of different levels may have different signs!).

Table 1.

Solvent	Fluorescence		Resonance Raman effect	
	quantum yield	τ_e, s	ω, cm^{-1}	I^S
Benzene	0.7	$3 \cdot 10^{-9}$	1340	5000000
Acetone	<0.03	$<10^{-10}$	1338	6000000

The lines due to the Raman overtones ($\nu - k\omega$) under conditions remote from resonance are so weak that they are rarely susceptible to observation. However, as resonance is approached, their intensity may increase sharply--to a greater extent the higher the order of the overtone k and they may form a complete progression[9,159,160]; this is possible for those fully symmetrical atomic vibrations which modulate the electronic transition frequencies ν_e.[9,161-163] Such progressions were observed for the first time in the resonance Raman spectra of diphenylpolyenes[138] and subsequently of many other compounds[164-166]; thus fifteen overtones have been observed in the spectrum of I_3^- ions[42] and 25 in that of iodine[142,167]. If the decay of the electronic oscillator is rapid, then Rayleigh scattering continues to predominate in the resonance spectrum with a smooth decrease of intensity within a series of $k\omega$ overtones[9,156,168-172] (and with a gradual broadening due to the broadening of the rotational and isotopic structures and finite vibrational k states[42,173-177]; see, however, Howard and Andrews[178]). In other cases the smoothness of the decrease may break down[9,179-182].

The measurement of the frequencies of the resonance Raman overtones led to new possibilities for the determination of the coefficients of the mechanical anharmonicity of the vibrations[142,156,170,176] and for the revision of the frequencies and the force fields in molecules[183]; data were obtained for metal–metal[156,184], metal–halogen[160,185], etc. bonds.

The lines of the non-totally symmetric ω_{as} vibrations proved to be the most intense in the Raman spectrum only in very rare instances; this has been observed for pyrazine on excitation with light at wavelengths in the vicinity of the $n \rightarrow \pi^*$ band[186], certain metalloporphyrins on excitation with light corresponding to the long-wavelength $\pi \rightarrow \pi^*$ band[187-191], and a few other compounds[192-196]. According to Kettle et al.,[197] the high ω_{as} intensity for $Mo(CO)_6$ can be accounted for by the fact that, when the CO bond is extended, the polarisability increases along the bond and decreases at right angles to it. However, there is no doubt that the symmetry properties of the resonance level e are of primary importance. Progressions in $k\omega_{as}$ overtones have not been observed experimentally, although in principle they are not ruled out in the presence of a high anharmonicity and for large differences between the shapes of the $E(Q)$ potential energy curves for the ground and excited electronic states; in a few isolated instances it has been possible to observe a single $2\omega_{as}$ overtone in the resonance Raman spectrum[198-200].

Another characteristic feature of the resonance spectra is the possibility of the appearance of vibrational line with inverse (degree of depolarisation $\rho \rightarrow \infty$) or anomalous ($3/4 < \rho < \infty$) polarisations. These include the very intense lines of certain non-totally symmetric a_{2g} vibrations in the spectra of metalloporphyrins with D_{4h} symmetry (vibrations with turning motions of the atoms of the macroring)[190,201]; for other examples, see Refs. 202–207.

Inverse polarisation implies that the oscillating dipole induced by the electric field of the light wave along the direction of the field (x) is not modulated by the vibrations of the normal nuclear coordinate Q and does not contribute to the Raman effect, while the y-component at right angles to the field is modulated and gives rise to a Raman line. For this unusual situation to occur, the "vibronic interaction" (see Section VI) is not obligatory (cf. Refs. 208–210). We shall consider an example in a very simplified form. Two identical electronic oscillators rock slightly in the course of the intramolecular vibrations of atoms with retention of mutually perpendicular orientations[211] of the dipole moments of the $0 \rightarrow e$ transitions (see Fig. 1, the vectors M). The resultant x-component of the vibrations of the two electronic oscillators is then high but virtually unmodulated. On the other hand, the y-component is on average zero, but under certain conditions it may be actively modulated by the atomic vibrations; the extent of modulation is determined by the sum of the projections of two vectors corresponding to the change in the orientations (ΔM) and two vectors corresponding to the change in the amplitudes (δM) of the oscillations (caused by the change in the effective field). When the decay constant of the electronic oscillator is high ($\gamma_e > \omega$) or when the Raman effect is excited under conditions remote from resonance, the modulation of the orientations and amplitudes of the oscillations of the electronic oscillators takes place in phase and the sum of the four ΔM and δM vectors is close to zero; when $\gamma_e < \omega$ the phases of the modulation of the orientations and amplitudes of the oscillations do not coincide, as a result of which the annihilation of the four ΔM and δM

modulation components is disturbed; the spectrum of the y-component vibrations then contains the $\nu \pm \omega$ frequencies, i.e. Raman lines, although the ν frequency is absent.

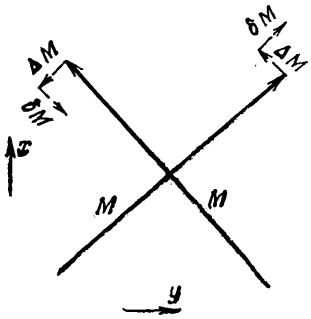


Figure 1. Evolution of the dipole moments of the transition in the course of atomic vibrations (model of a molecule with D_{4h} symmetry).

Anomalous polarisation has come to be invoked for the assignment of the resonance Raman lines to symmetry species [202,212,213], and to determine more precisely the symmetry of systems of conjugated bonds [151,190,214] and electronic transitions [204]. However, when the frequency ν changes, the quantity ρ for certain lines of porphyrins and other compounds [205,215] changes from values characteristic of fully symmetrical vibrations ($< 3/4$) to larger values ($\gg 1$), which has not so far been adequately explained and has complicated the assignment of the lines. Additional data for the $\rho(\nu)$ relation may be found in a number of studies [216-221].

Thus the resonance Raman effect is characterised by very high intensity coefficients and in certain cases also by the appearance of progressions of overtones; in a few instances there is a possibility of the appearance of anomalously polarised lines.

The resonance Raman effect may be regarded as absorption of an $h\nu$ photon and simultaneous emission of an $h(\nu \pm \omega)$ photon with an altered energy. The concept of absorption, the intermediate excited state of the molecule, and emission as successive stages of the transformation of the photon corresponds to the resonance fluorescence process and has been invoked to describe the Raman effect [222, 223] in purely conventional terms.

Typical scattering differs from the usual (relaxed) and resonance fluorescence by the following features: (1) the shift of the exciting light line in the spectrum induces the same shift of all the Raman lines (cf. Ref. 67); (2) the width of each Raman line is determined mainly by the width of the exciting line but not by the contour of the absorption band [9,224] (cf. Ref. 225); (3) there is no afterglow and no rotational depolarisation (cf. Ref. 117, where a different terminology is used).

Resonance fluorescence may be excited under the conditions of exact resonance ($\nu = \nu_{ev}$) for a very narrow absorption band (for $\gamma_e < \Gamma$, where Γ is the half-width of the incident light band). Radiationless deactivation of the intermediate excited state of the molecule [226] leads to a broadening of the absorption band, to a decrease of the intensity of the secondary resonance emission (Schmid [5], p. 286), and to its modification as far as transition to typical scattering when $\gamma_e \gg \Gamma$. Thus it creates conditions for the occurrence of scattering while at the same time it behaves as a competing process.

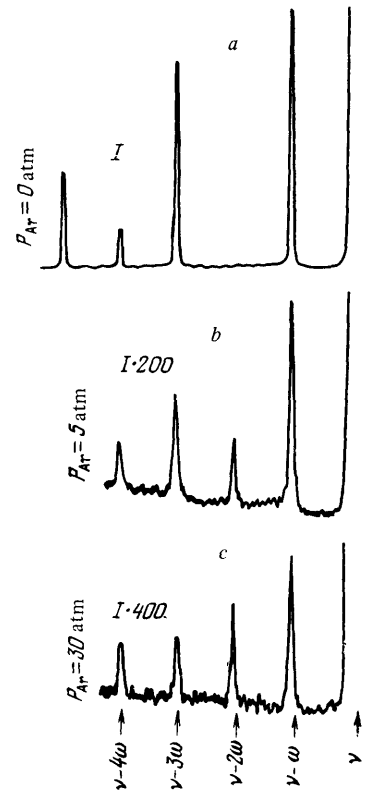


Figure 2. Spectra of the secondary emission of iodine vapour in the presence of argon; excitation by the 5017 Å line in the region of the discrete iodine absorption spectrum. With increase of argon pressure p_{Ar} from 0 to 30 atm, the intensity of the secondary emission falls sharply and there is a gradual transition of the intensity distribution in a series of overtones from that characteristic of resonance fluorescence to a smooth decrease of intensity characteristic of resonance Raman spectra [181].

The possibility, in principle, of a smooth transition from typical light scattering to resonance fluorescence with a gradual alteration of the difference $\nu_e - \nu$ and of the relations between the half-width of the incident light band Γ and the molecular parameters γ_e, ω, and the rotational frequency Ω has already been mentioned in a review [1]. Brilliant experiments, demonstrating the reality of the gradual disappearance of the dependence of the secondary emission line frequency on the frequency ν, [227] of the change in the energy distribution in the series of $0 \rightarrow k$ overtones (Fig. 2) [181], and of the evolution of the rotational structure of the lines with transformation of the Q-branch of the resonance Raman line into the R-branch of the resonance fluorescence line (Fig. 3) were carried out recently [14,181].

Certain data concerning the transformation of scattering into fluorescence as the resonance conditions are approached ($\nu = \nu_e$) for NO_2 and naphthalene and pyrazine crystals have been reported [228-230]. A resonance emission of an intermediate type, close to scattering, has been noted for solutions of diphenylpolyenes [138] and emission closer to fluorescence has been observed for ND_3 in the gas phase; in the latter case the half-width of the vibrational-rotational component of the absorption band (~ 2 cm^{-1}) was close to the half-width Γ of the incident light band [150].

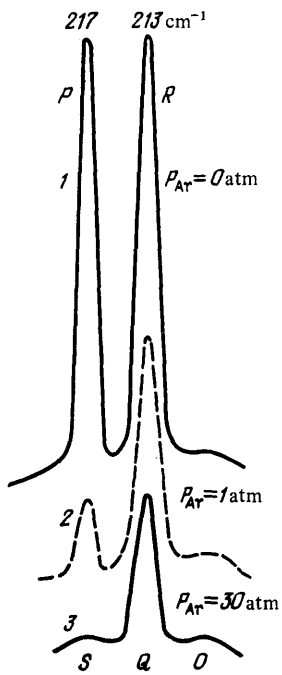


Figure 3. Modification of the rotational structure of the ~ 215 cm^{-1} iodine line with increased pressure of argon (transition from resonance fluorescence to resonance Raman spectra) [14]; the details have been omitted and the scale is arbitrary: 1) p_{Ar} = 0 atm, resonance fluorescence spectrum; 2) p_{Ar} = 1 atm, transitional spectrum; 3) p_{Ar} = 30 atm, resonance Raman spectrum.

Fig. 4 illustrates a very simplified example of the formation of the $I_{em}(\nu)$ secondary resonance emission spectrum in the region of a single $\epsilon(\nu)$ absorption band; the $I_{inc}(\nu)$ incident light line is shown continuous. The plot of the intensity of the secondary emission has two maxima; the left-hand and right-hand maxima symbolise resonance fluorescence and scattering respectively.

The problem of the boundary between scattering and fluorescence has been the subject of a lively discussion in the literature with invocation of various criteria [7,9,108,231-237].

IV. OTHER FORMS OF THE RESONANCE RAMAN EFFECT

Inverse Spectra

When light whose spectrum contains an intense ν line and a second component consisting of a broad band in a nearby region of the spectrum passes through a substance, weakening of the light flux may be observed predominantly in the region of the $\nu + \omega$ frequency (where ω is the frequency of the atomic vibrations in the molecule). This is because the "biharmonic" combination of the ν and $\nu + \omega$ components of the light field (which may be regarded as vibrations with beats at a frequency ω) may excite the atomic vibrations (along the normal coordinate Q) with a corresponding loss of light field energy provided that the derivative of the polarisability of the molecule $\partial\alpha/\partial Q \neq 0$. The components of the broad band, the frequencies of which are not equal to $\nu \pm \omega$, do not participate in such processes and are not weakened. The resulting selective (with respect to the spectrum) weakening of the light which has passed through the substance is called the "inverse Raman effect" or "inverse combination scattering" (although in essence it is not scattering). Resonance phenomena are observed for $\nu = \nu_e + \omega$ (when the intensity of the ω line increases) or when $\nu = \nu_e$ (when the intensities of all the Raman lines increase) [89,90].

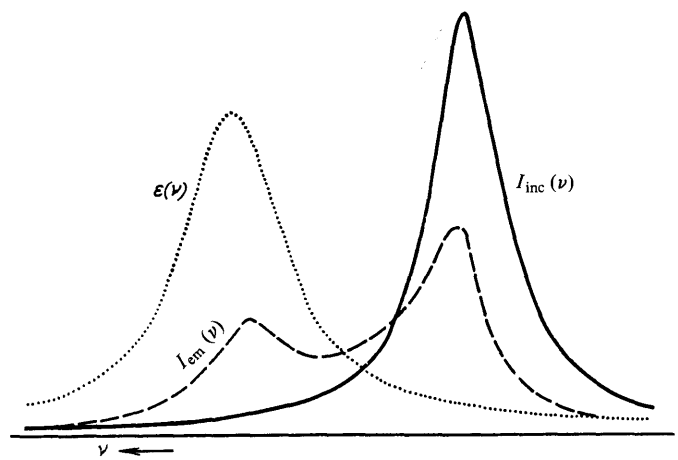


Figure 4. The $I_{em}(\nu)$ secondary emission spectrum (dashed line) with the oscillator vibrations excited in the vicinity of resonance (the simplest oscillator model); $\epsilon(\nu)$ absorption spectrum.

Coherent Active Raman Spectroscopy

When $\partial\alpha/\partial Q \neq 0$, a biharmonic light field, incorporating the ν and $\nu + \omega$ frequencies, is capable of exciting in the molecules of the given substance atomic vibrations which are concerted as regards phase over a fairly large volume of the specimen. The additional monochromatic excitation with a frequency ν^* is then actively modulated by these vibrations and gives rise to narrow directional beams due to displaced "scattering" at a frequency $\nu^* \pm \omega$ with a very

large quantum yield. This phenomenon can also be regarded as a kind of refraction of light. When $\nu^* = \nu_e$, conditions are created for the resonance transformation of light, which has been demonstrated for iodine vapour[91] and solutions of β-carotene[92] and other compounds[93], (Schmid[5], p. 740). The high intensity of the anti-Stokes ($\nu + \omega$) lines make it possible to investigate the Raman spectrum in the region where the interference due to fluorescence is a minimum.

The Resonance Raman X-Ray Scattering by Metal Atoms

This has been observed under conditions where the energy $h\nu$ (reaching 9000 eV) was close to the K-electron ionisation energy[66,71,72]. Under these conditions, the absorbed photon causes the transfer of an electron from the K-shell to the conductivity band, while an electron from the L-shell fills the resulting vacancy in the K-shell, which is accompanied by the emission of a resonance Raman effect photon; the final state of the atom is determined by the presence of an additional electron in the conductivity band and of a vacancy in the L-shell.

For details about the possible applications and other forms of the resonance Raman effect, see the literature quoted in Section I. A common feature of all types of the resonance Raman effect is the high probability of the transformation of photons and the high sensitivity of the methods.

V. PRINCIPAL TRENDS IN THE DEVELOPMENT OF THE THEORY OF THE RAMAN AND RESONANCE RAMAN EFFECTS

Various aspects of the theory of the Raman effect excited under conditions close to and remote from resonance have developed vigorously in recent years. Firstly, the ideas concerning the mechanism of light scattering by molecules with excitation of vibrational and rotational states have been extended and specified in greater detail. A tendency has arisen to establish quantitative relations between the Raman line intensities and other physical and chemical properties of the molecule. Secondly, new fields and methods have been described (for example, the method of differential spectroscopy). Significant advances have been made in all these aspects of the theory.

The intensity of the mth Raman line excited by a monochromatic light flux of constant and moderate intensity can be determined from the set of all the Cartesian components of the derivative of the polarisability with respect to the normal nuclear coordinate $\partial\alpha/\partial Q \equiv \alpha'$; without going into details, one can assume that the intensity is proportional to $(\nu - \omega)^4 |\alpha'|^2$. In the simplest version of the semi-classical theory[1,9,144] the quantity α' consists of contributions by all the levels (e) of the electronic excitation of the molecule:

$$\alpha' = \text{const} \cdot \sum_e \left[\frac{f'_e}{z} - \frac{2f_e\nu_e\nu'_e}{z^2} \right] = \sum_e (b_e^* + a_e^*) \qquad (1a)$$

or

$$\alpha' = \text{const} \cdot \sum_e \left[\frac{(M_e^2)'\,\nu_e}{z} - \frac{M_e^2(\nu_e^2 + \nu^2)\,\nu'_e}{z^2} \right] = \sum_e (b_e + a_e), \qquad (1b)$$

where $z = \nu_e^2 - \nu^2 + i\nu\gamma_e$, ν is the frequency of the incident light, M_e, f_e, and ν_e are the matrix elements of the dipole moment, the oscillator strength, and the $0 \rightarrow e$ electronic transition frequency, and γ_e is the decay constant; each level e is regarded as an integral hole (without taking into account the vibrational-rotational structure) and the frequency ν_e corresponds to the absorption band maximum; here and henceforth a prime denotes derivatives with respect to Q. The terms b_e (or b_e^*) are determined by the modulation of the values of M_e (or f_e) by the atomic vibrations and the terms a_e (and a_e^*) are determined by the modulation of ν_e; the latter arises when electronic excitation entails a change (Δ_e) in the equilibrium interatomic distances and Q.[1] Non-totally symmetric vibrations (for which $\Delta_e = 0$) cause the modulation of the M_e (or f_e) values only (if one disregards local electronic excitations), but for overtones both mechanisms of the modulation of α are important. The intensity of the overtones[238] is determined by the highest derivatives of α with respect to Q.

A method for the determination of the mechanism of modulation, employing a more marked dependence of the Raman line intensity on the frequency ν under the conditions of the modulation of the electronic transition frequency ν_e, was proposed a long time ago[239,240]. Despite the imperfection of the experimental technique, it was then possible to show that both types of modulation, i.e. both terms, a_e and b_e, may play an important role and that, as resonance is approached, the relative importance of the a_e term increases[145,240]. Little reliable information has yet been obtained on these problems. Some workers[6,241] do not take into consideration the a_e terms [the reasons for this being stated (or not)[134] with reference to an experiment, or to intuition[242]].

Incidentally the term a_e has not been entirely correctly transformed into the expression $[1 + (\nu/\nu_e)^2][1 - (\nu/\nu_e)^2]^{-2}$ and has been used in this form[243-248] to extrapolate α' to $\nu \rightarrow 0$ (according to the authors[248,249], this leads to a "more correct" value of α').

Eqns. (1) can be regarded as the result of certain simplifications in the Kramers–Heisenberg–Weisskopf formula. The latter has also served as the basis of a number of other versions of the theory. The appreciable differences in the formulation of the fundamental expressions and the contradictory estimates of the role of different factors as well as inaccuracies and errors in individual instances may make it difficult to become acquainted with the extensive relevant literature; certain explanations are therefore useful.

The familiar Albrecht formula in its initial form[250] took into account, like the Placzek polarisability theory (despite the assertions of Chao and Lippincott[241] and Schulman and Detrano[251]), only the modulation of M_e, i.e. the factor M'_e (the term b_e). Later[252] account was taken also of the modulation of ν_e (the factor ν'_e, the term a_e) and a more complete agreement with Eqn. (1) was achieved. The origin of the dependence of M_e on Q, i.e. of the derivative $\partial M_e/\partial Q = M'_e$, was specified in greater detail on the basis of the idea that the wave functions φ of different electronic excitation levels e and s are mixed on passing from the equilibrium configuration of the molecule ($Q = 0$) to the non-equilibrium configuration ($Q \neq 0$) during atomic vibrations ("vibronic interaction"[31,222,250,252-255]). The coefficients of the mixing of the wave functions h_{es} are specific to each vibrational mode; it has been suggested[256-258] that h_{es} should be greater the larger the alteration in the frequency ω on electronic excitation.

We shall elucidate the above statement concerning the "vibronic interaction" by a simple example. We shall assume that, for the equilibrium positions of the atoms, the $0 \rightarrow e$ electronic transition is forbidden; on deformation of the molecule by the nth normal vibration (i.e. for $Q_n \neq 0$), the wave function φ_e is modified as a result of the "admixture" of the wave function of another electronic

level s, the transition to which $(0 \rightarrow s)$ is allowed; the oscillator strength f_e for the deformed molecule will then prove to be non-zero and during atomic vibrations the "admixture" of φ_s and the quantity f_e (and hence M_e) will be actively modulated, contributing to the intensity of the Raman line[250,264]. In the simplest case where only two electronic excitation levels e and s are involved and in the absence of the modulation of ν_e and ν_s, one must assume that $f'_e = -f'_s$; one then obtains from Eqn. (1) the multiplier

$$F_B = \frac{\nu_e \nu_s + \nu^2}{(\nu_e^2 - \nu^2)(\nu_s^2 - \nu^2)},$$

the square of which should describe, according to Ziegler and Albrecht[104,250], the $I(\nu)$ relation.

In the general case one must take into account the mixing of the φ for all the levels e and s. Thus, instead of the single quantity M'_e for a single level e in Eqn. (1), one should introduce the complete matrix of the coefficients h_{es}, which is particularly complex in the case of overtones, because it includes higher-order coefficients (cf. Refs. 222, 223, and 259). The problem has been simplified by Warshel and Dauber[280] in essence at the price of partial neglect of the mixing of the wave functions. A realistic estimate of certain coefficients h_{es} has been achieved in only isolated instances[254,257,261]. The quantities M'_e and f'_e can be determined, in principle, from the analysis of limited sections of the absorption spectrum and are known for many simple molecules[262]. Both procedures, with introduction of M'_e and the mixing coefficients h_{es}, may be useful in the study of the mechanism of the Raman effect. However, examination of the set of all the Cartesian components M'_e makes it possible to take into account not only the "vibronic interaction" and h_{es} but also the contribution of the turning motions of individual fragments of the molecule.

Formulae for specific instances of excitation before and after resonance and between two absorption bands have been obtained[241,242,263]. They correspond to neglect of the term a_e and the unjustified introduction into the initial expression of resonance denominators of the type $|\nu_e - \nu|$ instead of $(\nu_e - \nu)$ and cannot be treated as correct.

Like all other formulae where the level e is regarded as an integral whole, Eqns. (1) are suitable in the resonance region only for very high values of γ_e on excitation to the region of broad structureless absorption bands; in the presence of vibrational structure one must take into account the contribution of the individual sublevels v, which, generally speaking, can be achieved on the basis of both classical and quantum theories[9,239,264].

We shall make use of the latter and shall quote in a very simplified form the expression for the matrix element of polarisability, which facilitates the determination of the term-by-term correlations with Eqn. (1b):

$$\alpha_{0k} = \frac{2}{hc} \sum_e \left[M_e^2 \sum_v \frac{\nu_{ev} A_{0v} A_{vk}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}} + \sum_v \frac{\nu_{ev} B_{ev}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}} \right] = \sum_e (A_e + B_e), \quad (2)$$

where ν_{ev} is the frequency of the $00 \rightarrow ev$ vibronic transition (in cm^{-1}), A_{0v} and A_{vk} are the overlap integrals of the nuclear wave functions of the 00 and ev and of the ev and $0k$ sublevels, and $B_{ev} = \mathbf{M}_e^{0v} M_e^{vk} - M_e^2 A_{0v} A_{vk}$, where $\mathbf{M}$ (in contrast to M) have been constructed from the complete wave functions ψ and not from the purely electronic wave functions φ, the superscripts denoting the quantum numbers of the vibrational sublevels of the combining states. The quantities B_{ev} and B_e are associated with the coefficients of the expansion of M_e in a series in powers of Q or, in terms of a more drastic simplification, with h_{es} [see Krushinskii and Shorygin[264] as well as Eqn. (8) in the paper of Rousseau and Williams[117]]. The term A_e is, roughly speaking, proportional to Δ_e.

The intensity of the Raman line of the fundamental band $(k = 1)$ is proportional to $|\alpha_{01}|^2$, the intensity of the first overtone $(k = 2)$ is proportional to $|\alpha_{02}|^2$, etc. For the fundamental, the terms A_e and B_e corresponding to each level e approximately correspond to the terms a_e and b_e of Eqn. (1).

According to Eqn. (2), the line intensity reaches a maximum when the frequency ν coincides with any component ν_{ev} of the structured absorption band; the excitation spectrum then has a series of maxima, the intervals between which are equal to the vibration frequencies of the atoms in the electronically excited states (whereas in the Raman spectrum itself the intervals in the progression of $k\omega$ overtones are determined by the frequency ω of the atomic vibrations in the ground electronic state); for very small[265,266] shifts Δ_e (and for a small anharmonicity of the atomic vibrations in the electronically excited state), only two maxima remain in the vicinity of the frequencies ν_{e0} and ν_{e1} (for the first overtone, in the vicinity of ν_{e0} and ν_{e2}; cf. Ref. 267). In complex molecules one cannot rule out the possibility of the separation of the $I(\nu)$ maxima with frequencies ω of "foreign" modes[254,268].

Owing to the difference between the signs of A_{vk}, the contributions of the sublevels v to A_e have different signs[239], which leads to a more pronounced $I(\nu)$ relation for Raman lines compared with Rayleigh scattering, particularly in the case of overtones, where there is a possibility of a repeated alternation of signs in a series of v sublevels[9] (a similar result in the semiclassical theory is determined by the higher powers of the resonance denominators). The neglect[269,270] of the integrals A_{vk} or of the differences between their signs is unjustified.

The difference between the signs of the contributions of different electronic levels e is associated with the difference between the signs of Δ_e (and also M'_e).[239,264] For a specific frequency of the incident light, this can lead in individual instances to the "annihilation" of the contributions of different levels e with weakening or complete disappearance of the Raman line, i.e. to the appearance in the excitation spectrum of an "anti-resonance" band (see the data for naphthalene[200], CdS,[271,272] and other compounds[115,273,274]; cf. Refs. 275–277). The appearance of anti-resonance owing to the different signs of the terms A_e and B_e for a single level e has already been examined[264].

The calculation of the values of $A_{0v}A_{vk}$ for all the sublevels v is fairly complex[168,180,278-280]. In order to simplify the task, it has been suggested that the entire sum with respect to v [see Eqn. (2)] be expanded in a series[107,275,281] in powers of $\nu_e - \nu$; then[107] $A_e \simeq [(\nu_e - \nu)^{-2} - \omega(\nu_e - \nu)^{-3} + \ldots]$. However, under conditions remote from resonance, this procedure leads to the same results as the more compact Eqn. (1) and in the region of resonance it gives rise to a diverging or a slowly converging series and loses its significance. The expansion[282] in powers of $\nu_{e0} - \nu$ gives rise to an even worse convergence. The above series[107] yields a more marked $I(\nu)$ relation for Raman lines with low frequencies which can actually occur only in certain special cases (approximately the same may be said about the $I \propto \omega^2$ relation obtained by Warshel and Dauber[280]).

Peticolas et al.[283] obtained a formula for the Raman intensity without summation with respect to v but with a resonance denominator of the type $(\nu_e - \nu)(\nu_e + \omega - \nu)$; in the region of a single electronic excitation level e it gives rise to two resonance points, ν_e and $\nu_e + \omega$, and therefore

in the vicinity of resonance it is suitable only for a very low deformation Δ_e of the molecule on electronic excitation; the two resonance points then correspond to the frequencies ν_{e0} and ν_{e1}. The same may be said of the formulae of Kobinata[259] and Nafie et al.,[223] designed for the region of resonance, which cannot be justifiably applied to iodine molecules with their large value of Δ_e.

The employment of such formulae is more appropriate for crystals, where Δ_e is as a rule very low and a vibrational structure is not usually observed for discrete electronic levels. However, the latter led to certain other misunderstandings. The appearance of two maxima in the region of one level e (for $\nu = \nu_e$ and $\nu = \nu_e + \omega$) was interpreted as the manifestation of resonance with the incident photon ($h\nu$) and with the scattered[76,77,116,284,285] photon $h(\nu + \omega)$. In fact the usual resonance takes place, in the first instance with the purely electronic $00 \rightarrow e0$ transition, which is clearly visible in the absorption spectrum, and in the second case with the vibrational satellite corresponding to the $00 \rightarrow e1$ transition, which is very weak but which gives a high quantum yield for the Raman line. Double resonance[285-287] must be interpreted in the same spirit—as the resonance with two partly overlapping sublevels $e1$ and $s0$.

On excitation of the resonance Raman effect in the region of an absorption continuum, arising from an electronic transition to a repulsive state or a state with rapid decay, the line intensities may be determined from Eqns. (1) and (2) with the corresponding constants γ_e or by means of other[226,288-290] suitable variants, for example by integration of the contributions from all the elements of the profile of the continuum without the introduction of a decay constant (as is done in the determination of polarisability by the Kramers–Kronig method)[159,291-294]. In any case, the knowledge of the form of the $\epsilon(\nu)$ continuum is insufficient for the calculation of the resonance Raman intensity.

The above formulae describes the smooth increase of the Raman intensity as ν approaches the region of maximum absorption in the continuum and the decrease of intensity on further increase of ν. However, according to Laplante and Bandrauk[295], here there should be whole series of maxima with decrease of intensity between them down to zero. This conclusion is incorrect and arises from the use of ideas about the $E_e(Q)$ "potential energy curve" for the repulsive state without taking into account the effect of the uncertainty principle when the effective lifetime of the intermediate state τ_{eff}, which limits the time over which emission of scattered radiation with transition of the molecule to the $0k$ state can occur; this time is longer the smaller the slope of the $E_e(Q)$ curve for $Q = 0$.

Above we were concerned with the usual cases to which the adiabatic approximation is applicable. The influence of non-adiabatic conditions on the intensity of the resonance Raman effect and on the excitation spectra has been considered[107,296,297].

In order to calculate the intensities of Raman and resonance Raman lines for specific molecules by Eqns. (1) and (2), it is necessary to know a set of parameters, which can be determined, in principle, from electronic absorption spectra or calculated theoretically[9,260,298,299]. In more primitive versions of the theory semiempirical relations and simplified molecular models are introduced instead of Eqns. (1) and (2). Below we shall consider briefly the methods of calculation employed, which will be arranged in order of increasing research value and rigour.

Applequist and Quicksall[300] calculated $\partial\alpha/\partial Q$ for methyl halide molecules using the Silberstein theory, which has been known for a long time and which assumes that each atom X in the molecule is polarised directly by the electric field of the light wave and by the field of the dipoles induced by light at the neighbouring atoms Y—the "partners" in chemical bonds; this additional polarisation naturally depends on the interatomic distances q_{X-Y}, which is described by the increments $\partial\alpha_X/\partial q_{X-Y}$. The authors[300] assumed that this model elucidates the mechanism of the Raman effect to a greater extent than the model with $\partial\alpha_{X-Y}/\partial q_{X-Y}$ chemical bond increments (see below), in which the "interaction of the dipoles induced in atoms is neglected". In reality neither model (nor the concept of resonance structures[301] and Pauling's oscillations between them[302]) can claim to explain the mechanism of the Raman effect, but the model with bond increments is closer to reality (it reflects, albeit implicity, the involvement of two-centre molecular orbitals and not individual atomic orbitals).

The zeroth approximation of the valence-optical scheme assumes the additivity of the polarisabilities of individual chemical bonds—"independent" molecular fragments. Three increments of α and three increments $\partial\alpha/\partial q$, corresponding to three Cartesian components, one of which coincides with the direction of the bond, are attributed to each bond (for example, C=C, C–Cl, O–H). Strictly speaking these increments have no physical significance even in those cases where their empirical selection leads to satisfactory results for molecules which are most consistent with the additive scheme (saturated hydrocarbons under conditions remote from resonance); in connection with the proof described in an earlier review by the present author[1] (p. 707), one may also refer to new interesting data concerning the splitting of the electronic levels of alkanes[303]. At the same time the possibility of adapting the valence-optical scheme are much wider than in the case of Silberstein's model. However, its use for compounds such as TiI_4, $SnBr_4$, and other coloured compounds[176,197,304] with non-local levels e lacks any justification.

In Lippincott's scheme a purely empirical selection of $\partial\alpha/\partial q$ increments is replaced by a semiempirical calculation[305] but with limitation to a single Cartesian component per bond, which naturally greatly diminishes the possibility of adaptation. The scheme is based on a very primitive one-dimensional model—an electron in a field with two identical infinitely narrow potential wells at the sites of the two atoms forming the chemical bond; here one can imagine an electronic excitation involving a transition between states with symmetric and antisymmetric wave functions; the frequency of the transition naturally diminishes as the bond is extended and the polarisability increases. In conformity with the assumptions made, the derivative of polarisability for $\nu = 0$ in the resulting formula (see, for example, Nagarajan[305] and p. 713 in the earlier review[1]) is proportional to the chemical bond order n. The formula has been used fairly widely for approximate estimates of bond orders from Raman intensities and for converse purposes; for example, a significant degree of π bonding has been noted[243,247,249] in $TiCl_4$ and VCl_4 molecules and in CrO_4^{2-} and MoO_4^{2-} ions. Estimates of bond orders made it possible to refine the force constants[306] for PF_5 and other molecules.

Fontal and Spiro[307] recently proposed a simplified expression for single bonds: $\partial\alpha/\partial q = 0.1\chi q_0^3 n$, where χ is the electronegativity of the atoms and q_0 the equilibrium bond length. On this basis, the authors[307] reached conclusions about the bonds in bridged complexes and about the degree of covalence of certain coordinate bonds.

In the first approximation of the valence-optical (additive) scheme refinements are introduced

in the form of additional empirically selected increments attributed to the influence of adjacent chemical bonds and valence angles. With the aid of a standard set of conventional increments (main and additional increments), it is possible to describe the intensities of the Raman lines for various molecules with "weakly interacting" bonds under conditions very remote from resonance. Thus, using 12 parameters of C–H and C–C bonds, determined from the Raman spectrum of cyclohexane, a satisfactory description of the spectrum of polyethylene was achieved[308]. Koenig and Bigorne[309] examined the $Ni(CO)_4$ spectrum and the additive scheme was supplemented by the separate contribution of the lone electron pair of the oxygen atom $\partial\alpha_{lp}/\partial q$.

The use of quantum-chemical LCAO-MO methods to calculate molecular wave functions and frequencies ν_e with subsequent evaluation of α_{01} or $\partial\alpha/\partial Q$ is much more promising and is of greater intellectual value than the computational procedures examined above. Quantum-chemical methods have been used for ethylene, acetylene, and certain other molecules[260,298,299,310], but in most cases only within the framework of the conventional problem of the influence of a static field[311-313].

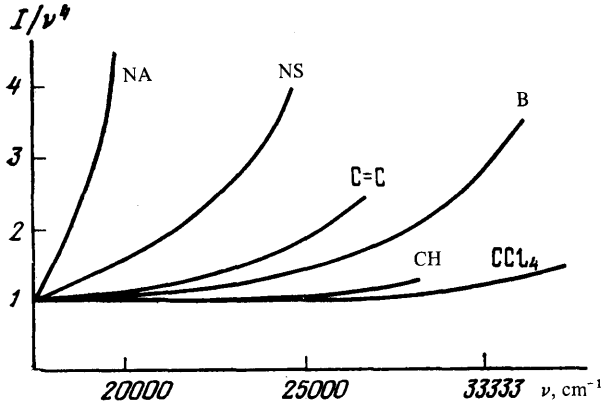


Figure 5. Deviations from proportionality between I_S and ν^4 with increase of the frequency of the exciting light ν and as resonance is approached; the values of the quantities compared are assumed to be unity at $\nu = 18000$ cm^{-1}; NA = *p*-nitroaniline, Raman line of the nitro-group; NS = *p*-nitroanisole, Raman line of the nitro-group[145]; (C=C) = line corresponding to the vibrations of the C=C bond in mono-olefins[240]; B = 992 cm^{-1} benzene line[104,314]; CH = 802 cm^{-1} cyclohexane line[314]; CCl_4 = 313 cm^{-1} carbon tetrachloride line[318,319].

VI. THE EXCITATION SPECTRA OF RESONANCE RAMAN LINES

When the spectra of colourless compounds are excited under conditions where the absorption bands are very remote from the incident light frequencies ν, the intensity of all the Raman lines increases smoothly with ν in proportion to the factor $(\nu-\omega)^4$ (see data for cyclohexane[314] and others[315-317]). It followed from the semi-classical theory that, under conditions somewhat less remote from resonance ($\nu_e - \nu < 40000$ cm^{-1}), the intensity may increase much faster owing to the simultaneous increase of α'. This was confirmed by experiments with olefins, ketones, and other compounds with single and conjugated π bonds. These experiments initiated systematic research into excitation spectra, undertaken at one time at the Karpov Physicochemical Institute[10,240]. One of the first results was the demonstration of a large contribution of the modulation of ν_e by the symmetrical vibration of the *p*-nitroaniline nitro-group on excitation by light corresponding to the long wavelength part of the $\pi \rightarrow \pi^*$ absorption band. Data for several compounds are presented in Fig. 5.

Further studies on *p*-nitroaniline[145,320,321] yielded an idea about the changes in the intensity coefficient I^S of the line due to the nitro-group over a wide range of frequencies ν [see Fig. 6, where the lg $I^S(\nu)$ relation is presented; the continuous line corresponds to the direct experiment and its extrapolation, shown as dashed lines, were constructed on the basis of analogies with other data]. With decrease of $\nu_e - \nu$ from 20 000 to 0 cm^{-1}, the intensity I^S increases by a factor of several thousand, in approximate agreement with the contribution of α_e^*; the form of the $I(\nu)$ relation permits an estimate of the decay constant as ~ 2000 cm^{-1}.[322] We may note that, at the frequency corresponding to the same $\pi \rightarrow \pi^*$ absorption band, one may expect only slight changes in the intensity of the C–H Raman lines, which are more closely associated with the $\sigma \rightarrow \sigma^*$ bands in the far ultraviolet.

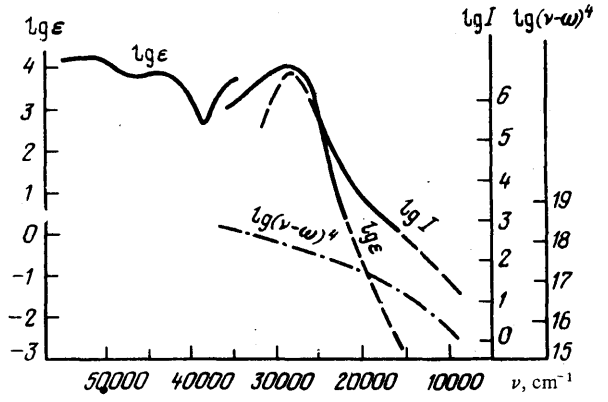


Figure 6. lg $I(\nu)$ nitro-group line excitation spectrum and absorption spectrum of *p*-nitroaniline (solutions in benzene)[145,320,321].

The approximate coincidence of the $I(\nu)$ and $\epsilon(\nu)$ maxima was observed not only for *p*-nitroaniline but also for the majority of other compounds with broad absorption bands; but a deviation by 300–800 cm^{-1} in either direction has been observed for bromine[322,323], solutions of iodine[324,325] and dimethylaminoazobenzene[326], and in many other instances, particularly for overtones[21,142,327].

Bobovich and coworkers[328,329] believe that the $I(\nu)$ maximum must be located in the region of the $00 \rightarrow e0$ transition, i.e. at the beginning of the absorption band [experimental data, see Schmid[5], pp. 284, 340], which is possible, in principle, only in certain special cases—with partial superposition of the bands due to different electronic transitions[324,325,331], when there is marked dependence of γ_{ev} on v, for certain low values of Δem, etc. The explanation of the causes responsible for the divergence of the $I(\nu)$ and $\epsilon(\nu)$ maxima given by Michaelian et al.[276] is incorrect and has been obtained on the basis of a simple exclusion of the contribution of the short-wavelength part of the absorption

band; the interpretation of Friedman et al.[322] does not differ greatly.

An example of a compound with a low decay constant ($\gamma_e < \omega$) and a distinct vibrational structure of the absorption band is provided by the diester EtOOC–$(CH=CH)_6$–COOEt. Fig. 7 illustrates the dependence of $\lg I^S/(\nu - \omega)^4$ on ν for the 1562 cm^{-1} Raman line due to the C=C vibration (the results of a direct experiment are shown by a continuous line); the curve is continued by dashed lines based on analogies with other similar compounds[138,338]. Together with experimental data, the results of calculations are presented for those cases where the intensity is determined by (1) the term b_e in Eqns. (1) of the semiclassical theory (modulation of f_e) and (2) by the formula of the quantum theory taking into account the contributions of individual sublevels ev subject to the assumptions corresponding to $f'_e = 0$ (dashed lines). The values of $\lg I^S/(\nu - \omega)^4$ for $\nu = 5000$ cm^{-1} were assumed to be unity; $\nu_e = 25\,520$ cm^{-1} and $\gamma_e = 250$ cm^{-1}.

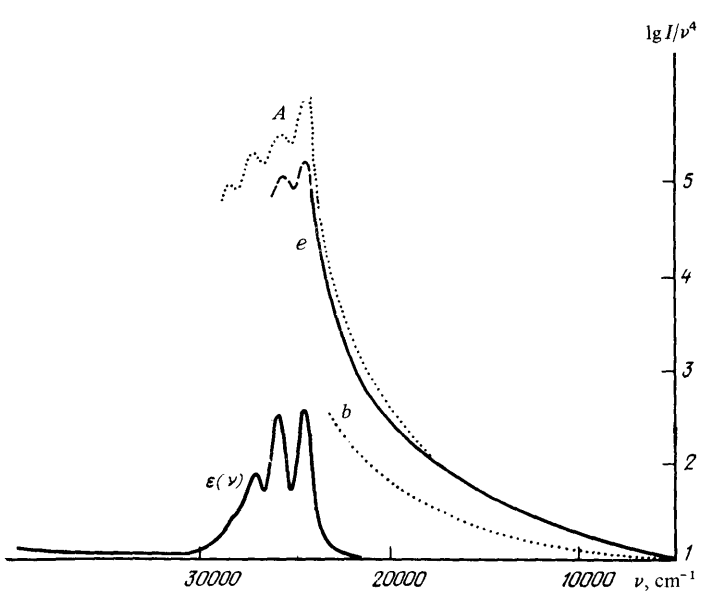


Figure 7. Relative changes in I/ν^4 for the C=C line of the diester (see text) as the region of resonance is approached; e—experimental data; A—calculated data with allowance for the term A_e only; b—ditto with allowance for the term b^*_e (modulation of f_e).

The term a^*_e of the classical theory and the A curve virtually coincide outside the region of resonance and agree with experiment much better than the term b_e and a little better than the term a_e, which shows that the contribution of the modulation of f_e is small. On excitation in the region of the components of the ev fine structure, the semiclassical theory is known to be inapplicable and the A curve, obtained within the framework of the quantum theory, agrees with experiment only qualitatively—it does not reflect the presence of several modes in the ev fine structure. Under conditions remote from resonance, either the contribution of A_e or that of the first absorption band is of secondary importance. We may note that, in the vicinity of resonance, the intensity of the diester line increases much faster than that of the p-nitroaniline line, which is due to the much smaller decay.

During recent years experimental studies have been made on the $I(\nu)$ relation for the Raman lines of many organic and inorganic compounds in the vicinity of resonance[50,243,247,317,329–336] and in the region of resonance corresponding to a structureless absorption band[56,145,148,329] [see also Schmid[5], pp. 328–337, etc.]; in the region of the band with an explicit vibrational structure studies have been made on polyene compounds[147,335–338], metalloporphyrins[202,254,261], haemoglobin derivatives[187], MnO_4^{2-},[168] and others[339–341].

Studies on certain totally symmetric vibrations of diphenylpolyenes[336], nitroaniline[277,321], $TiBr_4$,[342] MnO_4^- ions[159], and other species[160,245,276] led to the conclusion that the modulation of M_e (the term B_e) predominates. The predominance of the modulation of ν_e has been demonstrated for lines due to carotene[335,338], aminoazobenzene[326,343], diethylcyanine[344], haemoproteins on excitation with light corresponding to the Soret absorption band[187,345], nucleotides[99], SnI_4,[275,342] CrO_4^{2-} ions[36], MnO_4^{2-} ions[168], iodine[324,325], and other species[219,246,268,346] in the vicinity or in the region of resonance, as well as benzene[104], butadiene[317], and others[186,347] outside the region of resonance. On excitation with light corresponding to one absorption band, the C=C Raman line of the tetracyanoquinodimethane anion corresponds to the modulation of ν_e and, on excitation with light corresponding to another band, it corresponds to the modulation of M_e.[348] The data for phenazine, pyrazine, and PtI_6^{2-} ions indicate the modulation of ν_e by totally symmetrical vibrations and the modulation of M_e by antisymmetric modes[177,186,349]. According to Schmid et al.,[350] the asymmetric (b_{3g}) vibration line of anthracene corresponds to the frequency multiplier of the term A_e!

Unfortunately the number of experimental points[351,352] on the $I(\nu)$ curves and the information about the electronic absorption spectra and the constants γ_e employed[277,352,353] were in many cases quite inadequate and the set of electronic transitions taken into account was fairly arbitrary[160,241,245,263,276,333,342] and in addition was almost always restricted to the long-wavelength part of the spectrum. Nevertheless a more detailed analysis indicates the great importance of the range 1000–2000 Å[104,316]; thus, according to Ziegler and Albrecht[104], the most effective band for the 992 cm^{-1} Raman line of benzene is much more remote (~ 1200 Å) than the nearest intense absorption band (1830 Å).

Nevertheless, the set of all available data, including the more pronounced $I(\nu)$ relation for overtones[14,139,142] (and for the majority of lines due to $0 \rightarrow 1$ symmetrical vibrations compared with lines due to asymmetric modes[291]), the similarity in the sets of frequencies ω observed in resonance Raman spectra and in the fine structure of absorption bands, as well as the results of certain quantum-chemical calculations[298,299] show that the term A_e predominates in the vicinity of resonance for the majority of lines due to totally symmetrical vibrations.

As an example, we may mention the results of calculations of the intensity and scattering activity (which does not include the multiplier ν^4)[1,7,15], obtained[298] by the CNDO/C method for the Raman lines of ethylene in all three versions, which demonstrate the relative contributions of M'_e and ν'_e under conditions remote from and close to resonance (Table 2); Table 3 provides information about the contributions of the factor ν'_e for the six most important levels e, the first of which corresponds to the excitation of π electrons and the remainder correspond mainly to the excitation of σ electrons[298].

Calculation of the intensity of the C=O line of benzaldehyde[310] under conditions remote from resonance indicates the predominance of the factor M'_e for the majority of the levels e.

Table 2. Calculation of the scattering activities for the C–H (3019 cm^{-1}) and C=C (1623 cm^{-1}) ethylene lines.

ν, cm^{-1}	C–H			C=C		
	calc. with allowance for different factors			calc. with allowance for different factors		
	M'_e	ν'_e	M'_e and ν'_e	M'_e	ν'_e	M'_e and ν'_e
8 000	67	3	93	8	6	14
16 000	77	4	107	8	19	27
24 000	132	5	152	9	520	510

Table 3. Calculation of $\nu'_e M'^2_e$ for the C–H and C=C ethylene lines.

ν_e, eV	$\nu'_e M'^2_e$		ν_e, eV	$\nu'_e M'^2_e$	
	C–H	C=C		C–H	C=C
6.41	0.4	−5.6	13.40	−1.6	−1.2
8.93	−2.4	−1.6	15.75	−13.6	1.6
12.50	−1.6	0.4	16.13	−1.2	−0.4

The excitation spectra of the Raman lines resemble electronic absorption spectra (see the examples quoted in the literature[24,254,329,340]), but for many complex molecules the $I(\nu)$ bands are much narrower and the excitation spectrum reveals the concealed structure of the broad absorption band formed as a result of the superposition of many components (Fig. 8).

Summarising, the following may be said. The positions of the Raman lines in resonance Raman spectra characterise the ground electronic state of the molecule; the excitation spectra of resonance Raman lines provide information about electronically excited states, which frequently cannot be secured by measuring the absorption spectrum.

The excitation spectra have been used to solve a very wide variety of problems underlying in one way or another more advanced stages associated with the study of molecular structures and chemical transformations: 1. The elucidation of the mechanism of the Raman effect (the type of modulation, the contribution of the Frölich interaction in semiconductors[22,82] etc.), and test of the validity of particular variants of the theory. 2. The separation of resonance Raman and fluorescence lines. 3. The determination of the role of various absorption bands and of their contributions to the intensities of specific Raman lines[99, 317,334,354]. 4. The determination of the concealed structures of absorption bands (see Section VII). 5. The elucidation of the type, location, symmetry, and energy of electronic excitation[156,184,187,340,346,355,356]. 6. The determination of the width of the forbidden gap in the components of binary semiconductor compounds. 7. The derivation of information about the geometry of the molecule and the frequencies ω in electronically excited states[100, 103,257,258,334]. 8. The estimation of the lifetime of the excited state τ_e in the case of a non-uniform broadening of the adsorption band[290] (which cannot be done on the basis of the absorption spectrum). 9. The construction of the $E_e(Q)$ potential energy curve when bands due to different electronic transitions are superimposed[289]. Other applications of the excitation spectra as well as individual examples will be given in the next section.

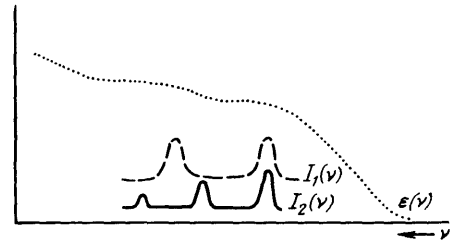


Figure 8. Excitation spectra of two Raman lines (ω_1 and ω_2) of a hypothetical complex molecule.

There is no doubt that the joint investigation of absorption and resonance Raman excitation spectra is extremely useful and improves the effectiveness of spectrochemical studies.

VII. CHEMICAL APPLICATIONS OF RESONANCE RAMAN SPECTROSCOPY

The applications of resonance Raman spectroscopy are based on determinations of the frequencies ω, the molar intensities I, the degrees of depolarisation ρ, and $I(\nu)$ line excitation spectra. The experimental data are used on the basis of theoretical generalisations and empirical relations which determine the relations between the parameters of the spectra and molecular structure.

The ways in which the information about the Raman and resonance Raman line frequencies is used are in principle the same; the most important trend in this field involves the detection of specific structural groups in the molecule and the determination of their positions as well as the characterisation of the state and rigidity of the chemical bonds. However, resonance Raman spectra give rise to the following additional possibilities: 1. An extension of the set of frequencies ω susceptible to measurement as a result of the discovery of lines forbidden by the usual selection rules (for example, inversely polarised lines). 2. The detection, identification, and investigation of the structures and chemical transformations of trace impurities[357], biologically active compounds present in very low amounts, impurity centres in crystals, etc. 3. The study of the structure of short-lived intermediates. 4. The characterisation of monomeric products in the absence of association at very low concentrations (10^{-4}–10^{-8} M[326,337]). 5. The determination of the frequencies of overtones (and the components of their isotopic structure) and of the coefficients of the anharmonicity of the interatomic potentials with the corresponding revision of the molecular force field, dissociation energy, etc. 6. The isolation of the frequencies ω and characterisation of specific chromophoric groups in complex molecules. According to Baierl

et al.,[68] the moments of inertia and centrifugal deformation constants may be determined from rotational resonance Raman spectra no less accurately than from electronic absorption spectra.

The available information about the line intensity makes it possible, in principle, (1) to characterise the change in the polarisability of molecules on extension of specific chemical bonds and, on this basis, the bond order, (2) to investigate the kinetics of the reactions of unstable species and intermediates, (3) to determine quantitatively the content of microimpurities, the distribution of molecules with respect to orientation[28,61], the distribution of inhomogeneities on the surface of a solid under static conditions and in the course of chemical reactions, as well as equilibrium constants at low concentrations, (4) to demonstrate the involvement of particular atomic groups in conjugation and in the given type of electronic excitation, (5) to determine the location of the active centre responsible for the formation of an intermediate complex or the transition state, and (6) to determine, when the assignment of the resonance Raman lines is known, the type and location of electronic excitation (and conversely)[143,340,352,358].

We shall now consider in greater detail individual aspects and specific examples. In very complex molecules containing thousands of atoms the number of normal atomic vibrations is extremely large. The detection and assignment of individual lines and the derivation of useful information from the spectrum excited under conditions remote from resonance are difficult or impossible. However, when the Raman spectrum is excited in the region of the absorption band of a specific chromophoric centre, a very limited set of frequencies ω for the centre, susceptible to interpretation, is isolated. Thus, when the resonance Raman spectrum is excited with light corresponding to the long-wavelength absorption band of haemoproteins, it is possible to observe the intense lines due to the metalloporphyrin system without any interference by the protein fragments which incorporate more than 99% of the total number of atoms of the metalloprotein. The same situation arises on excitation of the lines due to the thiouracil residue of modified RNA.[98] If the molecule contains several different unconnected chromophoric centres, it is possible to excite the resonance Raman spectra of each independently. By varying the frequency of the exciting light, it has been possible to isolate consecutively the resonance spectra of systems with different numbers of conjugated double and triple bonds in polymers; thus the statistics of the distribution of conjugated systems has been characterised[359] in terms of the number of π bonds in such systems and data have been obtained on their structures and transformations as the temperature is altered.

A high intensity of the low-frequency lines due to the vibrations of bonds with a heavy atom has been noted for many compounds, the intensity increasing further on excitation with light corresponding to absorption bands associated with charge transfer along the bond[184,355,360,361]; an example is provided by the Ni–C line in the $Ni(CO)_4$ spectrum[309]. The intensification frequently extends to the lines for the atomic groups of the ligand adjoining the heavy atom. These factors have been used to assign the Raman lines (or the absorption bands corresponding to the wavelength used to excite the resonance Raman effect) and in structural studies[143,156,362,363]. Thus the enhanced intensity of the lines due to the phenolic group of tyrosine in the resonance Raman spectrum of Fe-transferrin[364] and their normal intensity for stellacyanin[365] served as a basis for inferring the structure of the region of active centres in these metalloproteins; the spectrum of stellacyanin indicates a quasi-tetrahedral coordination of copper with participation of nitrogen atoms, which can be inferred from the intensification of lines due to the amide group.

A study of the resonance Raman spectra of $NaClO_3$ crystals irradiated by a beam from an electron accelerator revealed the formation of two types of unstable ClO_3 radicals differing in their positions in the crystal lattice and in the kinetics of their decomposition; the excitation spectra showed that definite (different) regions of the ~ 5500 Å broad absorption band correspond to these types; the authors[38,39] note that, without an appreciable resonance intensification, the observation of the Raman lines would have been impossible owing to the rapid decomposition and low concentration of the radicals.

The resonance Raman lines of impurity centres (O_3^- ions) formed in chlorates on γ-irradiation have a multiplet structure and the excitation spectra of individual components of the multiplets are different. The results indicated the formation of four types of ion with different orientations; they made it possible to estimate their distribution with respect to orientations, to derive information about the mechanism of the radiolysis, and to demonstrate the formation in the first stage of ClO_3^{2-} ions, which decompose by several paths[40]. The formation of metastable O_2 molecules with a slightly reduced bond rigidity on radiolysis has been demonstrated by the same method[38,39].

The study of excitation spectra has shown that the intensity of the C=C lines of alkenes and dienes is determined mainly by the $\pi \rightarrow \pi^*$ long-wavelength absorption band (~ 1800 Å and correspondingly ~ 2200 Å[240,317]), the changes in interatomic distances in the $\pi \rightarrow \pi^*$ transition being rather significant and corresponding to $\Delta C{=}C = 0.08$ Å and $\Delta C{-}C = -0.055$ Å in the case of tetrachlorobutadiene[103].

The separation of the contours of broad absorption regions into zones corresponding to different vibro-electronic transitions on the basis of resonance Raman excitation spectra has frequently proved very effective[142,366,367]. Thus it has been possible to observe weak components, which are virtually indistinguishable on the basis of $\epsilon(\nu)$ curves, for example the long-wavelength electronic transition in polyenes[368-370], to detect in the broad contour of an absorption band several electronic transitions in those cases where only one had been postulated[215,355], to determine the frequency of the purely electronic $00 \rightarrow e0$ transition and other ev components[215,340,371,372] [thus a single C≡N line gave rise to seven $I(\nu)$ maxima at the wavelength corresponding to the absorption band of tetracyanoquinodimethane radical-anions, the maxima being assigned to elements of the vibrational structure[366]], to isolate absorption regions referring to very similar compounds present simultaneously in a complex product (for example to different haemoproteins, to conjugated systems of different lengths in polymers and to incompletely equivalent impurity centres in crystals) and to characterise further their structure, to determine the structure of the conductivity band of crystals which is difficult to investigate[24,35,85], and to determine the location of the lines due to dipole-forbidden exciton transitions in the absorption spectrum[285].

Thus measurements of excitation spectra assist in a more complete interpretation of the absorption spectra and hence extend the scope of structural analysis.

An exceptionally high sensitivity of the intensity to conjugation conditions has been noted also outside the region of resonance in a number of studies. Certain molecules (and ions) hardly differ as regards the frequencies ω and ultraviolet absorption spectra but have very different resonance Raman line intensities; examples are provided by tetracene[373] and triphenylmethane (Schmid [5], p. 300)

anions and cations. When complexes with weak bonds are formed, the frequencies ω of the components hardly change, while I^S may increase by several orders of magnitude (complexes of tetracyanoethylene with aromatic hydrocarbons[374], etc.). A sharp increase of the Raman line intensities has been described for certain colourless compounds in contact with molecules of dyes[94,6] and with a metal[375,376], which is probably due to the breakdown of the localisation of electronic excitation.

Moschalski and Schmid (see Schmid[5], p. 46) showed, using excitation in the visible part of the spectrum, that the stretching vibration line due to the two non-conjugated C=C bonds in norbornadiene has a reduced intensity owing to the interaction of the π bonds through space; with increase of the distance between two C=C bonds in other hydrocarbons, the line intensity approaches the normal value. Evidence for conjugation has been noted in the spectra of cyanoepoxyethane[377] and π-electron systems linked by –NH– and –S– bridges (Ph–C≡C–S–C≡C–Ph, etc.[378]) and has been studied in detail for a large number of PhX molecules. The data obtained for the intensity of the polarised line of the benzene ring at ~ 1600 cm^{-1} have been used to determine the angle of rotation of the plane of the benzene ring in the presence of steric hindrance[336,379] and to investigate the relations with Hammett and Taft constants[1,420]. The contributions of n,π-conjugation in such systems are considered by Epshtein et al.[380] to be fairly small and masked by the influence of certain differences between the vibration modes.

The determination of resonance Raman line frequencies has been used to solve a very wide range of problems. For example, it made it possible to estimate the degree of charge transfer and the charge distribution in certain donor–acceptor complexes[381] and ions[382], having resolved controversial questions concerning their structure, to determine the rigidity of the bonds between F-centres and crystal lattice atoms[43], to establish an appreciable double bond character of the C–N linkage in the p-phenylenediamine radical-cations[30], to discover a significant redistribution of electron density from phenyl groups to the main chain in polyphenylacetylene[25], to obtain new data on the structures of iodine–amylose complexes, indicating the presence of chains comprising ~ 28 iodine atoms in which it is possible to distinguish three-atom units[383], to show that the impurity centres in natural pale-yellow fluorite crystals are O_3^- ions[37], to determine the differences between the valence states of two ruthenium atoms in a pyrazine complex[356], etc.

The mechanism of the reactions of diphenylethylene following its adsorption on silica gel has been studied recently; the appearance of new resonance Raman lines in the first stage was attributed to the formation of a carbonium ion, which is rapidly converted into a π-complex, the spectrum being modified further (see Schmid[5], p. 298).

According to certain data[384,385], it is possible to distinguish and characterise azo-quinonoid and intermediate forms of acid–base indicators (aromatic azo-compounds) and to refine ideas about the mechanisms of their reactions at varying pH and low concentrations, which correspond to the conditions under which they are applied in practice. According to Machida et al.,[384] when alkaline solutions of Methyl Orange are acidified, the azo-group is protonated and the indicator is converted into acid forms close to a quinonoid type; on the other hand, the azo-forms of analogous hydroxyphenylazo-compounds persist. The formation of Methyl Orange complexes with serum albumin modifies the colour changes of the indicator; however, the study of the spectrum disproves the conclusion that the azo-form undergoes a *trans* → *cis* transition and that a proton is transferred from the protein[386].

The resonance Raman spectra of Tropaeolin O reflect three stages in its colour changes and consecutive protonation as the pH is reduced. Saito et al.[385] determined the equilibrium position under conditions corresponding to the simultaneous presence of several forms (whose total number is 8) at all the stages of the colour changes and characterised the state of the π-electron system in each form. According to the results, the triply charged anions (judging from the spectrum, they resemble an azo-structure but with appreciable delocalisation of excess electron density) are converted into dianions, which may be present in three forms, including the quinonoid form, then into monoanions (quinonoid and azo-forms), and finally into neutral molecules which are said to exist[385] in a zwitterionic "hybrid" form similar to the quinonoid form.

The appearance of the intense 160 cm^{-1} line in the spectrum of the dimeric cations of p-phenylenediamine on excitation with light corresponding to the charge-transfer absorption band served as the basis for assigning this line to the intermolecular vibration in the dimer and for the corresponding estimate of the force constant of the bond between the dimer components (0.82×10^5 dyn cm^{-1})[387].

An exact determination of the frequencies of the overtones has been used to find the dissociation energy of I_2^- ions in a matrix (20 kcal $mole^{-1}$),[178] the heat of atomisation of O_3^- ions (153 kcal $mole^{-1}$), the electron affinity of ozone molecules (42 kcal $mole^{-1}$),[44] etc.[184]

Resonance Raman spectra are widely used to investigate metalloporphyrins and, in the words of Yamamoto et al.[388] "constitute a highly effective means for the investigation of haemoproteins". Experiments have shown that when the resonance Raman effect is excited by light corresponding to the $\pi \rightarrow \pi_1^*$ absorption band (~ 5000 Å), the lines of a number of non-totally symmetric vibrations with participation of the C–C and C–N bonds of the macroring are particularly strongly intensified; on excitation with light corresponding to the Soret band (~ 4000 Å), mainly the lines of the fully symmetrical modes, including low-frequency modes with participation of bonds involving the metal atom, are preferentially intensified[255]. Certain characteristic resonance Raman lines have been used successfully as spin indicators and indicators of the state of oxidation of the metal atom[129,360,389], of the breakdown of coplanarity of the metalloporphyrin system[188], and of the change in the quaternary structure of a protein[207]. The positions of these lines in the spectrum are associated with the conjugation conditions and the rigidity of the π bonds in the macroring[218,339,390].

We shall now present several examples. The study of the frequencies of the indicator lines led Kitagawa et al.[391] to the conclusion that there are two types of low-spin ferrohaemoproteins differing in the type of bond with the fixed (axial) ligand: with coordination of the lone electron pair of the ligand atom to the unfilled d_{z^2} orbital of the Fe atom (cytochromes) and with $d\pi$(Fe)–π^*(Lig) interaction (oxyhaemoglobin, myoglobin, nitrosohaemoglobin). The indicator line for the interaction with ligands indicates the replacement in stages of the sixth ligand in the haem groups in ferrocytochrome c_3 as the pH is raised[392]. In certain high-spin ferri-haemoproteins (chloroperoxidases) the frequencies of the indicator lines are reduced, which indicates a shift of electron density from the axial ligands to the porphyrin system accompanied by population of the anti-bonding π^* orbital and the corresponding decrease of the rigidity of the π bonds[393]. Indicators of the breakdown

of coplanarity (reflecting the conjugation conditions in the metal–porphyrin system[218]) demonstrate, according to Felton et al.,[206] the displacement of the Fe atom from the plane of the four nitrogen atoms in oxidised hydroperoxidases by ~ 0.5 Å; indicators of the spin state disprove the conclusion that there is an equilibrium between states with 5/2 and 3/2 spins.

The presence of the characteristic intense 1373 cm^{-1} line confirms that protohaemin incorporates Fe^{3+} ions; the ~ 1500 cm^{-1} line is characteristic of a high-spin state of iron and of a non-planar structure of the chromophore, but in the complex with imidazole it is located in a higher position and indicates a low-spin state and a planar structure for the same oxidation state of iron[345].

The study of anomalous forms of haemoglobin[394] showed that the position of the Fe atom relative to the plane of the haem group in α-chains is not altered when iron in the β-chain is reduced and thus the quaternary T-structure is retained.

The possibility of recording the changes in the resonance Raman spectra of haemoglobin as the partial pressure of oxygen is altered has been noted[53]. It is suggested that the resonance Raman effect may serve as the basis of apparatus for clinical studies on blood (see Schmid[5], p. 212).

The study of the resonance Raman spectra of oxyhaemerythrin—an oxygen transferring agent of a non-haem type—made it possible to exclude structures with equivalent oxygen atoms from the five proposed versions of the structure; in azidomethaemerythrin all three nitrogen atoms are located in non-equivalent positions[395]. Eight models of oxyhaemocyanine, an oxygen-carrying metalloprotein from the haemolymph of molluscs, have been considered in the literature. The frequencies of the resonance Raman lines correspond to a non-planar structure in which the bound oxygen exists in the form of a peroxide ion and the copper atoms are present in the bivalent state[396-398].

Carey and Schneider[399] noted that resonance Raman spectroscopy is a very useful instrument for the investigation of the mechanisms of enzymatic catalytic reactions and may yield extensive information about the modifications of individual atomic groups on formation of intermediates when enzymes interact with coloured substrates; furthermore, the deformation of the substrate is one of the factors responsible for the increased rate of reaction. According to the authors, the intermediate formed in the reaction of papain with an ester containing the α-benzamide group has a sharply different resonance Raman spectrum compared with the initial and final products[400,401]. The spectrum indicates changes in the acetyl group and a rearrangement of the benzamide group of the substrate:

$$-NH-CO-Ph \rightarrow -N=C\begin{matrix}Ph\\ O-X\end{matrix}.$$

New data on the structure of enzyme–inhibitor complexes have been obtained in a number of studies[402-404]. For example, it has been shown that the sulphonamide group in certain derivatives of sulphonamidoazobenzene in complexes with carbonic anhydrase B is ionised and that the coplanarity of the azobenzene group is significantly distorted.

Resonance Raman spectroscopy has been used to determine the types and locations of enzyme modifications. It has been established that, when carboxypeptidase reacts with arsanilic acid, the tyrosine-248 group is modified; the reaction of carboanhydrase with diazobenzenesulphonamide results in the diazotisation of the histidine residue (see Schmid[5], p. 206).

Carey et al.[406] investigated the applications of resonance Raman spectroscopy in immunochemistry, particularly for the determination of the active centres of antibodies and the structure of complexes with haptens. The resonance Raman spectra of such complexes reflect the perturbations induced by the interaction with the protein, including the changes in the state of ionisation and conformation of individual fragments. The authors investigated the lines of bound coloured haptens (dinitrophenylazonaphthalenedisulphonic acids), characterised the changes in conformation, and demonstrated a decrease of the amount of double bond character in the N–O linkage in both nitro-groups as a result of the influence of the specific charge distribution in a particular fragment of the antibody. The studies established the changes in conformation favouring contact with the active centres of antibodies isolated from mouse tumours.

Resonance scattering has been used to detect traces ($\geqslant 0.0001\%$) of polyene compounds in thermally degraded specimens of poly(vinyl chloride). On excitation of the spectrum at different frequencies, systems with different numbers of units were excited. Thus an increase of the average chain length of conjugated C=C bonds with increase of temperature and of the duration of heat treatment of the polymer has been demonstrated[357].

The spectra of the carapaces of live crayfish demonstrated the presence of astaxanthin bound to a protein[405]. Distinct lines of carotenoids were detected in the resonance Raman spectrum of the sciatic nerve of the frog[407]. The presence of β-carotene, bound in the membranes of erythrocytes (predominantly in cholesterol-depleted regions) has been demonstrated[408] and its content determined ($7 \times 10^{-4}\%$ relative to the weight of lipids); the increase of the intensity of the characteristic lines when the membrane is acted upon by trypsin and lysolecithin is regarded as an indication of the modification of the carotene molecules as a result of the decrease of the internal strain in the surrounding regions; sharp changes in intensity with increase of temperature above 17°C indicate changes in conformation (see Schmid[5], p. 178).

In Lewis's words, resonance spectroscopy is exceptionally effective in the study of visual processes. With the aid of resonance Raman spectroscopy, Lewis investigated the transformation of rhodopsin at different stages of the dark adaptation of a functioning eye[54,414]. New data have been obtained[118,409] for the structures of intermediate products in very rapid multistage transformations of bacteriorhodopsin—a photosynthetic system which ensures proton transfer via cell membranes of halophilic bacteria. Other examples in the field of biochemistry have also been described[401,410-420].

Resonance Raman spectroscopy has been used successfully to study the mechanisms and kinetics of electrochemical processes. The advantages of the method compared with infrared spectroscopy (higher sensitivity and the possibility of employing aqueous solutions and metallic electrodes), ultraviolet spectroscopy (a greater yield of information), and EPR (the possibility of studying ions, neutral molecules, and radical-ions) have been noted[62]; the method is suitable for the investigation of organic, inorganic, and organometallic electrosynthesis[63].

The ways of using resonance Raman spectroscopy to probe the atmosphere and to determine the substances contaminating air at heights up to 10 km (Raman radars), to determine from a flying aeroplane the presence of certain coloured components in air over the surface of the sea in order to estimate its bioproductivity[421-423], etc. are being investigated. The possibility of using

resonance Raman spectroscopy in the study of the atmospheres of other planets is not ruled out.

CONCLUSION

In recent years a major contribution has been made to the development of the spectroscopy of resonance light scattering by molecules and crystals. The improvement of the experimental techniques and theories and the study of correlations between the spectra and the structure of molecules and their physicochemical properties greatly extended the basis for a wide variety of applications of resonance Raman spectroscopy. According to the authors of a number of studies, "resonance Raman spectroscopy has become a powerful method for the investigation" of molecular structures[253], elementary excitations of the crystal lattice[35,424], biochemical processes[346], electronically excited molecular states[425], vibronic interaction[426] of polymers and oligomers with conjugated bonds[25], and haemoproteins[388] and has become "a powerful analytical tool"[331,337]. The method combines the high sensitivity characteristic of ultraviolet spectroscopy with the high resolution characteristic of microwave and infrared spectroscopy[28,62]; as regards the amount of information which can be derived, the method can be, in principle, superior to infrared and ultraviolet spectroscopy taken together. Despite the number of limitations of the method, many new useful data have been obtained with its aid in chemistry, physics, and spectrochemistry. The use of a more advanced technique (among others, for the measurement of the Raman line excitation spectra and for the investigation of the phenomenon by time scanning[9, 117,427,428]) will promote the development of new productive research fields.

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