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Raman Scattering and Conjugation

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CONTENTS

I.	Introduction	367
II.	General views on the nature of Raman scattering. Semiclassical theory	368
III.	Quantum theory of Raman scattering	371
IV.	Experimental observation of Raman resonance scattering spectra	372
V.	Characterisation of molecular fragments in the presence and in the absence of conjugation	373
VI.	Measurement of Raman line intensities. Symbols	374
VII.	Intensity of the Raman lines of simple molecules	376
VIII.	Intensity of the characteristic lines of the most important atomic groups	377
IX.	Effect of substituents on the spectra of compounds with C-C π-bond systems	378
X.	$n-\pi$ conjugation	379
XI.	$\pi-\pi$ conjugation	380
XII.	Conjugation in X--Y molecules	383
XIII.	Conjugation with a three-membered ring	383
XIV.	Systems with a bridging atom (Π-M-Z). $\sigma-\pi$-conjugation	384
XV.	Applications of Raman line intensity studies	386

This review presents the results of recent work on the nature of the Raman scattering of light and on the relation between the parameters of the Raman lines and other molecular constants; the problems encountered in applying line intensity data to studies of the interaction of atomic groupings in organic molecules are discussed in detail. Various types of conjugation are considered, including the effect of substituent atoms on π-bond systems (with special reference to the position of the atoms in the Periodic Table), and the possibility of characterising molecular fragments in the presence and in the absence of conjugation. 328 references.

I. INTRODUCTION

The study of mutual interactions of atomic groups in polyatomic molecules is one of the most important problems in organic chemistry. This approach offers a relatively compact description of a vast multitude of experimental data, and thus enables available data to be applied more effectively to the production of compounds possessing desired properties. It is no exaggeration to say that if the properties of complex molecules could be described by a simple additive scheme the whole of organic chemistry would be reduced to a set of tables of increments, similar to the table of refractive index increments. In practice, however, the number of compounds showing specific properties is almost inexhaustible —this arises from the mutual interactions of atomic groups, which are difficult to study partly because of the complexity of the overall picture and partly because of the limitations of the various methods of investigation. It is desirable, therefore, to carry out combined physical and chemical studies, including atomic vibration spectroscopy (Raman and infrared spectra).

The Raman spectrum consists of a set of lines with frequencies $\nu - \omega_m$, in the vicinity of the exciting line ν. The normal vibration frequencies ω_m of the atoms in the molecule can be used to determine the elastic coefficients of the chemical bonds and the interaction coefficients.

Recent advances in the techniques of Raman spectroscopy—in particular the advent of spectrometers using laser radiation (see Refs. 1-3)—have considerably extended the scope of the method. Spectra can now be obtained from crystalline powders [4-8], polymers [9,10], coloured compounds, and also from samples available in very small quantities (a few mg, and in some cases as little as 0.001 mg). [6,11-13] Line intensities have been measured with solid [5,7] and gaseous samples, and the resolution of closely spaced lines has been improved (see for example Fig. 1). The use of laser light facilitates measurements at low frequencies (see Fig. 2) and allows fast processes to be studied with measurement times of the order of a millisecond [14].

Contrasting the relative advantages of Raman and infrared spectroscopy, we note that the strongest lines in the Raman spectra of symmetrical molecules are those due to totally symmetric vibrations. In keeping with their polarisation, they show little broadening associated with a latent or apparent rotational structure [15,16], and their half-width usually lies in the range 2-20 cm^{-1}. [16-18,24] Conversely, the strongest bands in infrared spectra are those due to antisymmetric vibrations, and also those of strongly polar bonds, which are broadened not only by the rotational motions of the molecules but also by the greater sensitivity of their frequency to intermolecular interactions.

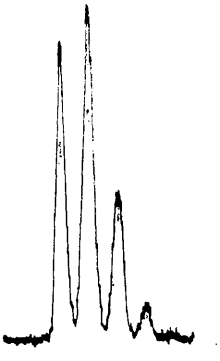


Figure 1. Fine (isotopic) structure of the ~460 cm^{-1} line of CCl_4 at 77°K.

Considering the differentials of the dipole moment $d\mu/dQ_m$ and $d^2\mu/dQ_m^2$ (where Q is the normal nuclear coordinate), we may conclude that the stronger an infrared spectral band is, the more likely it is to be broadened in the case of liquids [19]. Furthermore, overtones are relatively more intense in infrared spectra, and they give rise to more overlapping lines.

Whereas the frequencies observed in infrared and Raman spectra are largely duplicate information, the same is far from being true of the line intensities. It must be admitted, however, that most workers report only qualitative assessments of the intensity ratio of Raman lines for individual spectra: these are useful for assigning the lines, but they cannot be used to compare the lines of different compounds. A universal, objective scale of molar intensities, proposed [17] in 1940, defined the rational conditions for a quantitative comparison of the intensities of lines of different compounds, and made it possible to examine different groups of organic compounds.

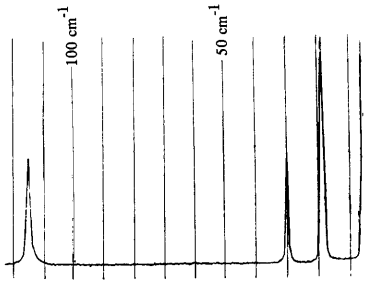


Figure 2. HgI_2 spectrum (He–Ne laser spectrometer). Curves kindly supplied by Dr. E. da Silva (France).

Molar intensity measurements are reproducible, and are an important characteristic of Raman lines. They offer useful additional information on the structure of molecules, on the properties of chemical bonds, on the mutual effects of atomic groups in complex molecules, on electronic excitation levels, on the vibrational modes associated with particular lines [15,16], and on the quantitative composition of mixtures of compounds [17,20,21,24]. Many interesting relationships have been established, and it has been shown that the intensity is one of the parameters most sensitive to conjugation.

This review is particularly concerned with applications of line intensity measurements to studies of the interaction of atomic groups: the relevant literature will be surveyed in the sections devoted to the nature of Raman scattering and to the interrelation between line intensity and other molecular constants.

II. GENERAL VIEWS ON THE NATURE OF RAMAN SCATTERING. SEMICLASSICAL THEORY

The basic Raman parameters can be described by classical theory, by quantum mechanics, or by quantum electrodynamics. Depending on the circumstances, it may be preferable to use one or other of these approaches, or to combine some of their features.

In studies of the line intensities (I_m) of colourless compounds it is usually possible to confine the discussion to the simplest variant of the classical theory, in which one considers the vibrations of the dipole $\mu(t)$ resulting from the polarisation of the electronic shell of the molecule by the field of the light wave. The intensity of the Raman lines depends on the depth of modulation of $\mu(t)$, produced by the vibrations of the nuclei, defined as $\frac{\partial\alpha}{\partial q}$. q_0 for diatomic molecules, and $\frac{\partial\alpha}{\partial Q_m}$. Q_{0m}, for polyatomic molecules, where α is the polarisability of the molecule, q is the change in interatomic distance, q_0 is the amplitude of the vibrational ground state, Q_m is the m-th normal coordinate of the nucleus, Q_{0m} and ω_m are the corresponding amplitude and frequency [22]. One can avoid the explicit use of the differentials of α by considering that I is defined by the difference ($\Delta\alpha$) between the values of α at the two extreme positions of the vibrating atoms; this gives almost the same result (slightly more accurate, in fact) [23]. For a discussion of the convergence of the power series $\alpha(Q)$ and of the contribution from the higher differentials of α the reader is referred to Krushinskii [59].

The relative intensity I_m of the Raman line of frequency $\nu-\omega_m$ (or, more briefly, of the "line ω_m") under normal experimental conditions† is proportional to

$$(\nu-\omega_m)^4(45\,\bar{\alpha}_m'^2+13\,b_m'^2)\,Q_{0m}^2; \qquad (1)$$

where ν is the frequency of the exciting light, $\bar{\alpha}'_m$ and b'_m are the mean value and the anisotropy of the tensor $\frac{\partial\alpha}{\partial Q_m}$. [22] A more detailed treatment can be found in the literature [22,25,26,27].

In the semi-classical theory of Raman scattering [28–30] each Cartesian component (x, y, z) of the differential of α with respect to Q_m is given as the sum of contributions from all the electronic excitation levels e:

$$\alpha'_{xm}=\text{const}\sum_e\left[\frac{f'_{xe}}{\nu_e^2-\nu^2+i\nu\gamma_e}-\frac{2f_{xe}\nu_e\nu'_e}{(\nu_e^2-\nu^2+i\nu\gamma_e)^2}\right], \qquad (2)$$

where the prime denotes a differential with respect to Q_m, f_{xe} is the oscillator strength, measured by the area under the u.v. absorption band for the $O\rightarrow e$ transition (for oriented molecules), ν_e is the frequency of the band maximum, and γ_e is the damping coefficient. Eqn. (2) can be rewritten in terms of the matrix elements of the dipole moment instead of f; in this case a somewhat different relative contribution of the first and the second term in the binomials under the summation sign is obtained, but their sum remains the same [12,16]. We shall consider only the more compact form of the expression, given in Eqn. (2). Without going into details, we note that the intensity (I_m) is given by the square of the modulus of α'_m: in the simplest case, $I_m\simeq\nu^4|\alpha'_{xm}|^2Q_{0m}^2$. In the general case all the Cartesian coordinates have to be considered. Lea's conclusion [31] that the semi-classical theory can deal only with the contribution from a single level and is applicable only to a one-dimensional model is quite unjustified.

Formulae (1) and (2) correspond to steady-state vibration conditions of the electronic oscillator: a definite value of the polarisability of the molecule corresponds to each value of Q_m. These conditions obtain either outside the resonance region or within the resonance region but in the presence of strong damping.

†Standard temperature, irradiation with unpolarised light, disordered orientation of the molecules, and observation at a right angle to the direction of irradiation.

According to Eqn. (2), Raman scattering occurs because both the oscillator strength (f_e) and the frequency of the electronic transition (ν_e) vary during stretching of a chemical bond[28-30]. Placzek's "polarisability theory"[22] takes account only of changes in f_e. The origin of the changes in ν_e is evident from Fig. 3, which shows typical potential energy curves for the ground state, $E_0(q)$, and for an electronically excited state, $E_e(q)$. In formula (2) the values of ν_e and ν'_e correspond to the equilibrium position of the nuclei, $q = q^{(0)}$; in Fig. 3 ν_e is given by the length of the vertical arrow $h\nu_{ev}$*, and ν'_e by the slope of the curve $E_e(q)$, which depends on the change (Δ) of the equilibrium value of q following electronic excitation. $d\nu_e/dq$ can be as high[30,32] as 10 000–100 000 $cm^{-1}/Å$.

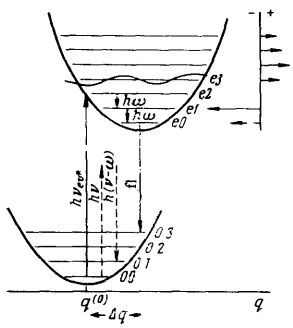


Figure 3. Optical transition model for a diatomic molecule.

From formula (2), and various experimental and theoretical data, we can draw the following conclusions:

1. There is a close relationship between Raman spectra and u.v. absorption spectra. I_m is related to the parameters of the u.v. absorption bands (mainly those in the long-wave region, which are stronger and have a latent or developed vibrational structure corresponding to ω_m, i.e. those with fairly large values of Δ.[16,28-30,33,34] Thus, the intensity is related to the geometry of the molecule in the excited state. The efficiency of particular electronic excitation levels (and the form of the function $I_m(\nu)$) can vary quite significantly for different Raman lines[28,35].

2. When $\nu_e - \nu > 50\,000$ cm^{-1} (aliphatic hydrocarbons under normal Raman excitation conditions), α' and α are practically independent of ν and of ν_e; the intensity of the Raman lines is very low (below the Rayleigh scattering level by a factor of several hundred), and is proportional to $(\nu-\omega)^4$. The Raman lines of cyclohexane[36] are typical of this type of line. The value of α is affected by only a few per cent as a result of nuclear vibrations.

3. When $50\,000 > \nu_e-\nu > 5000$ cm^{-1} (as in the majority of colourless organic compounds) I_m increases rapidly as $\nu_e-\nu$ decreases, both for a series of compounds with decreasing ν_e and for a single compound with increasing ν. On raising the frequency ν of the exciting radiation, the intensity increases faster than by the factor $(\nu-\omega)^4$ of formula (1), since the increase in α' is beginning to have an effect[12,32,33-43]. When several conjugated π-bond systems are present—at least in the case of totally symmetric vibrations—it is not surprising that the second terms in the square brackets of formula (2), containing the factor ν'_e, become dominant[12,32,33,43,44]. Under these conditions the depth of modulation of the molecular polarisability can be as high as 10–20% for small departures from resonance. The polarisability itself is often found to be higher (by 1–10%) than the value expected on the assumption of additivity.

4. When $\nu_e-\nu < 3000$ cm^{-1} (as in coloured compounds) we encounter resonance Raman scattering conditions, first observed in potassium p-nitrophenate[45-47]. This effect is characterised by a very high intensity (though re-absorption can occur under normal experimental conditions). According to Placzek (see Section 25 of Ref. 22), the Raman effect should be replaced by resonance fluorescence when the spectrum is excited within an absorption band. It has been shown[29,30,33], however, that this can only be true at very low damping γ_e (see Section III). Under conditions not very far from resonance it is likely that only one electronic level will be involved, which allows us to ignore the summation over all e in formula (2) and to consider only the contribution from a single electronic level. The imaginary part of α' plays an important role in the resonance region: it determines the depth of modulation of the imaginary part of the polarisability. The achievable depth of modulation of α can be judged by taking p-nitrodiethylaniline as an example: in this compound the difference ($\Delta\alpha$) between the polarisability values for two extreme positions of the vibrating atoms of the nitro group is of the order of 50 $Å^3$ for resonance excitation, whereas the polarisability of the molecule under the same conditions[23] is of the order of 150 $Å^3$.

The resonance denominators in the first and the second term under the summation sign in formula (2) are raised to different powers. Hence, using the function $I(\nu)$, we can identify the cases where either of these terms is predominant: in other words, whether the function $f_e(Q)$ or the function $\nu_e(Q)$ is responsible for the appearance of a Raman spectrum[48], and we can also assess the efficiency of a particular electronic excitation line towards the Raman line under study.

We shall consider the influence on $I(\nu)$ of a single electronic excitation level with large values of Δ_e and ν'_e and a large damping constant ($\gamma_e \gg \omega$) for $f'_e \simeq 0$. Because of the difference in the resonance denominators in the expressions for α'', α', and α,[29,30] the intensity of the overtone increases faster than the intensity of the Raman line of the fundamental as ν increases and the resonance region is approached, and the latter increases faster than the intensity of the Rayleigh line. (Hence, the contribution of Raman scattering to the total scattered intensity increases.) Close to resonance, damping becomes important and the intensity of all the above lines increases more slowly. It reaches a maximum near the maximum of the absorption band, and then begins to fall off (see, for example, Fig. 1 of Ref. 49). We should note that the two maxima in the $I(\nu)$ curve in the region of a single structureless absorption band shown in Fig. 26 of Ref. 25 and Fig. 1 of Ref. 50 are the direct result of the simplifying assumption made[25,50] to describe the electronic level (rectangular well).

A more complete description of the situation is shown in Fig. 4, where the following quantities are plotted: a) the outline of the absorption band $\epsilon(\nu)$; b) the real part of the polarisability Re $\alpha(\nu)$; c) vectors (broken lines) defining the complex polarisability (α) on the complex surfaces for several particular values of the frequency of the incident light (ν). Each of these originates from the position of the corresponding vector on the frequency scale. In this diagram, the projection of the vector on the horizontal axis is the real part of α, and the projection on the vertical axis is the imaginary part of α. Solid-line

arrows denote the complex *derivatives* of α for the same values of ν (the scales of α and α' are in arbitrary units).

The symbol $|\alpha|$ represents the amplitude of vibration of the electronic oscillator, corresponding to a frequency ν for the equilibrium position of the nuclei; $|\alpha + \alpha'|$ relates to one of the extreme positions of the vibrating nuclei; α' (or, more strictly, $\alpha' q_0$) defines the amplitude of the changes in α (occurring with a frequency ω), and the angle between $\vec{\alpha}$ and the horizontal axis is the phase difference between the oscillating field of the light wave and the induced moment $\mu(t)$.

Outside the resonance region, Raman scattering is determined by the amplitude modulation of $\mu(t)$—note that the directions of $\vec{\alpha}$ and $\vec{\alpha}'$ coincide in Fig. 4—and in the resonance region ($\nu \simeq \nu_e$) Raman scattering is determined mainly by phase modulation [23] ($\vec{\alpha}$ and $\vec{\alpha}'$ have different directions). In the latter case, expansion of $\mu(t)$ in a Fourier series gives a whole series of spectral lines $\nu \pm n\omega_m$, where $n = 0, 1, 2\ldots$ [51].

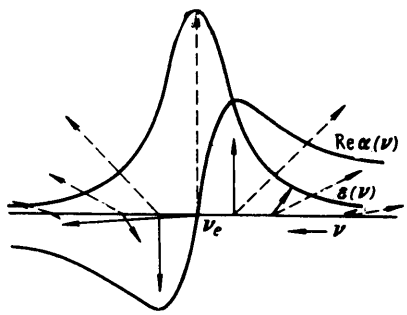


Figure 4. Complex values of α and α' for several values of the frequency ν in the region of the absorption band ($\gamma \gg \omega$, $f_e' \simeq 0$).

When $\nu \simeq \nu_e$, α' is real (see Ref. 25), whereas the contribution of the electronic level to α is imaginary. We must stress the fact that whereas only the real part of α contributes to refraction, both the real and the imaginary part contribute to the intensity of the Raman lines [23]. This is because the nuclear vibrations in different molecules have independent phases.

We have considered the case where ν_e' is the quantity which determines the amplitude of the Raman line. If $\nu_e' = 0$, but $f_e' \neq 0$, the Raman lines for the fundamental and the overtone will have identical $I(\nu)$ functions, coinciding with the corresponding function for the Rayleigh line. Under these conditions, only amplitude modulation of α is possible; as ν is varied, $\vec{\alpha}'$ will vary in the way indicated for $\vec{\alpha}$ in Fig. 4. A proportionality is then found [52] between $\epsilon(\nu)$ and $I(\nu)$, or [41] between $\epsilon(\nu)$ and $I(\nu)/(\nu-\omega)^4$. In general, such a proportionality can be expected for the sum of the intensities of all lines in the scattered spectrum [52]. Experiments on particular compounds with wide absorption bands have shown that $\epsilon(\nu)$ varies in the same sense as $I(\nu)$, [32,33,46] approximate (or exact [53]) proportionality being found in the region of strongest absorption [32].

Most of the existing experimental data on $I(\nu)$, particularly when far from resonance, are difficult to interpret because the u.v. absorption spectra have not been investigated over a sufficiently wide region. This explains also, at least in part, the conflicting conclusions which have been reported on the relative role of the factors f_e' and ν_e' (see Ref. 52–56 and comments in Ref. 57, 58).

A more convincing interpretation of $I(\nu)$ can be obtained in the case of compounds with a strong, isolated, long-wave absorption band. Thus, the intensity of the lines for the nitro group in a series of aromatic nitro compounds has been shown [32] to increase with ν very much faster than expected from f_e'. Even more revealing are the results for the esters of polyene acids (see Section XI), which include a very wide range of $\nu_e - \nu$ values (from 1000 to 30 000 cm^{-1}). [12] In this case it is clear that the factor ν_e' makes a contribution at least an order of magnitude greater than that of f_e' even at $\nu_e - \nu \simeq 10\,000$ cm^{-1}.

It follows from various other results (including fluorescence spectroscopic data) that Δ_e and ν_e' are usually different from zero in totally symmetric vibrations. In diatomic molecules, which have been most thoroughly investigated, it is usually found that $\Delta > 0$ and lies between 0.05 and 0.2 Å; f_e', on the other hand, is relatively small (see discussion in Ref. 59). Lastly, there is a striking agreement between the normal vibrations found in the fine structure of u.v. absorption bands and those found in resonance Raman spectra [11,34].

The form of $I(\nu)$ becomes more complicated if the terms contributed to α' by different electronic levels (or by the two terms for the same level in formula (2)) are of opposite sign [48,57,58]. In such cases, I_m can decrease and even vanish as ν increases over some range of values below resonance, and it can increase quite rapidly beyond that region. However, this behaviour has never been observed in practice; this is in keeping with the view that the contribution from f_e' is small, and can be of either sign, whereas ν_e usually decreases and the polarisability increases when a chemical bond is stretched.

Experimental confirmation has been obtained for the results of the semi-classical theory which predict different $I_m(\nu)$ functions for the different Raman lines of a given compound [35,36], steeper $I_m(\nu)$ functions for small γ, [11] particularly for overtones close to resonance at fairly large values of Δ_e [11,60–62] (but see Ref. 53), and many other effects.

The classical theory of Raman scattering in the simple form discussed above cannot deal with resonance radiation with $\gamma_e < \omega$, i.e. in the presence of vibrational structure in the u. v. absorption band (strictly speaking, when $\gamma_e < 2\nu_e' Q_{0m}$ [23]). These conditions are met, for example, in studies of polyacenes, polyenes, and polyynes. Under these conditions the electronic oscillations lag behind the displacement of the vibrating nuclei and cannot reach a steady state. "Forced" and "natural" vibrations of the oscillator become indistinguishable, and beats are produced by the continuous change in the frequency ν_e. [52,63]

In these circumstances the concept of polarisability of a function of nuclear coordinate, used [22] in the "polarisability theory", becomes meaningless. The polarisability can be replaced by a more general function [52], which is time-dependent, similar to the "transfer function" $K(\nu, t)$ used in electronics. This function is determined by solving the equation of motion of the electron, of frequency ν_e, modulated by the motions of the nuclei. Ultimately we obtain a set of Fourier components similar to the polarisability matrix elements used in quantum theory [51]. The most interesting feature of this new variant of the classical theory is its great similarity to the quantum-mechanical theory. In many respects, the general form of the absorption and emission spectra given by both theories is almost the same. It is incorrect to say that the classical theory is concerned with the frequencies of transitions between two continuous potential energy curves for the two electronic levels involved,

whereas the quantum theory deals with transitions between discrete electronic-vibrational sublevels: both theories predict a continuous absorption spectrum for high values of γ and a spectrum with a discrete vibrational structure for $\gamma < \omega$.[51,52]

A further generalisation of the classical theory to include the case of irradiation by a broad-band light source is given in Ref. 63 and 64.

III. QUANTUM THEORY OF RAMAN SCATTERING

The quantum theory of scattering deals with the probability of a change in the vibrational quantum number v, brought about by that part of the energy of the quantum of incident light $h\nu$ which undergoes changes and finally appears as scattered light. The probability of a change in v from 0 to 1 without a change in the electronic state (00 → 01 transition) is defined by the matrix element of the polarisability α_{01}.

It has been shown[23,30,48,52] that the concept of a total wave function ψ for a molecule, expressed as a product of nuclear (u_{ev}) and electronic (φ_e) wave functions, leads to an expression of the type of Eqn. (3):[65]

$$\alpha_{01} = \frac{2}{h}\sum_e \sum_v \frac{\nu_{ev} A_{0v} A_{v1}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}} M_{0e}^2 (1 + D_{ev}), \qquad (3)$$

where ν_{ev} is the frequency of the electronic-vibrational transition 00 → ev, in s^{-1}, M_{0e} is the matrix element of the dipole moment of the 0 → e transition, obtained from the electronic wave functions of the ground (0) and the excited (e) state, A_{0v} are the integrals for the combination of the nuclear wave functions of the sublevels 00 and ev, A_{v1} are the integrals for the combination of the sublevels ev and 01, D_{ev} allows for the dependence of M_{0e} on Q. The expressions for α_{00} and the other α_{0n} terms differ from Eqn. (3) only in respect of the subscripts after A. The resonance denominator can be averaged, and the summation with respect to v of the numerators can be replaced by the overlap integrals of u_{00} and $M(Q)u_{01}$, only if $\Delta_e \simeq 0$.

Fig. 3 shows, together with the potential energy curves, the vibrational sublevel systems 0v and ev (horizontal lines) which are considered in the quantum theory. $h\nu$ is a quantum of incident light (under resonance excitation conditions) which is transformed into a quantum of scattered light ($h(\nu-\omega)$). The frequency ν_{ev}* corresponds to the maximum of the absorption band of the compound ("Franck–Condon" transition, 00 → ev*). It is clear that the frequencies ν_{ev}, unlike the frequency ν_e which appears in Eqn. (2), cannot be treated as a function of Q (see comments in Ref. 54).

According to Eqn. (3), α_{01} is made up of contributions from several sets of v sublevels in the electronically excited levels. When the individual sublevels merge into a single wide band (for $\gamma_e > \omega$), formula (3) in no way loses its relevance. The contributions from ev sublevels lying above and below ev* have opposite signs (see right-hand side of Fig. 3): when the spectrum is excited far from resonance these contributions effectively cancel out, the summation over v is close to zero,[48] and the Raman line has a very low intensity. As ν approaches the value ν_{e0} the contribution from all the sublevels increases—particularly the lower ones. The compensation of the positive and the negative contributions is progressively lost, and there is a rapid increase in α_{01} and in the line intensity[48].

According to the present theory, Raman scattering results from the presence of a developed (or latent) vibrational structure in the absorption band ($\Delta_e \neq 0$), and also from the dependence of M_{0e} on v (or on Q).

The formulae of the quantum theory are quite different from those of the simple variant of the classical theory. However, when conditions are far from resonance, both sets of formulae predict almost identical intensity values provided that ν_e is taken to be the frequency at the *maximum* of the absorption band[57] (see also Ref. 42 and 66). Under these conditions[22], $\alpha_{01} = \frac{\partial \alpha}{\partial Q} Q_0$. The summation of the ev contributions with different resonance denominators in the quantum mechanical formula (3) corresponds to making allowance for ν_e' in the classical theory; allowing for the small difference in M_{0e} for the different sublevels (or for the parameter D_{ev}) is equivalent[48] to introducing the factor f_e' in formula (2).

Analysis of formula (3) allows us to characterise the secondary resonance radiation of light from various molecules, not involving intermediate transitions in the excited state, for different relative values of γ and ω and for different half-widths (Γ) of the incident light band.

Most of the experimental data on resonance Raman scattering, including those for nitro and nitroso compounds[46,47,49,67,68], relate to the case of $\gamma > \omega > \Gamma$ (excitation by a narrow line, very wide absorption band). Under these conditions resonance scattering differs from non-resonance scattering mainly in the greater line intensity of the former[52]; the relative intensity of the overtones can also be abnormally high.

For somewhat lower values of γ ($\omega > \gamma > \Gamma$ and $\Delta_e \neq 0$), when the absorption band has a developed vibrational structure, one of the characteristics of the normal scattering spectrum tends to be lost (unshifted lines are strongly predominant, and Raman overtones are very weak[69]). This is because a single ev vibrational sublevel makes an overwhelming contribution to the matrix elements of the polarisability α_{0n}. It is possible to find an overtone line with a higher intensity than the fundamental Raman line, and the latter can be stronger than the unshifted scattering line[52]. The secondary radiation acquires some of the features of resonance fluorescence ("transition phenomena of the first kind"). Spectra of this type have been observed in solutions of diphenylpolyenes[11] (Fig. 5) and esters of polyene acids[12] (see discussion in Ref. 27). On going to the conditions $\omega > \Gamma \simeq \gamma$, the similarity between resonance radiation and resonance fluorescence increases: the outline of the bands becomes very similar to the outline of the characteristic lines of the oscillator ("transition spectrum of the second kind"). The situation is illustrated in Fig. 6, and discussed in Ref. 69 and 328.

If γ becomes very small, and comparable with the rotational frequencies ω_{rot} ($\omega_{rot} > \gamma > \Gamma$), different rules apply to the changes in rotational quantum number and the depolarisation of the lines increases. In the first instance, only one rotational sublevel in the ev level can now contribute to α_{0n}, instead of two or three. The increased depolarisation is associated with the onset of "afterglow" under the conditions of molecular rotation. An example of this situation is given[86] by the excitation of the iodine vapour spectrum by the narrow argon laser line, which falls in the region of the fine structure of the I_2 absorption band. On moving still further towards the condition $\omega_{rot} > \Gamma > \gamma$, the predominant spectrum of the secondary radiation should show all the characteristics of resonance fluorescence (including a well developed afterglow).

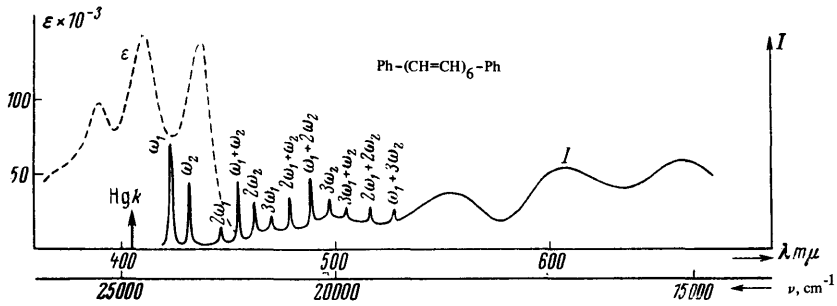


Figure 5. Transition spectrum of the secondary radiation from a solution of diphenyldodecahexaene (full line). The narrow Raman lines are on the left, the fluorescence bands on the right. The exciting Hg*k* line is shown by an arrow. The absorption spectrum is shown by a broken line [11].

On the whole, we may conclude [63] that, depending on the spectral composition of the incident light and on the properties of the oscillator, the secondary radiation can show the typical features of light scattering or of fluorescence, or of an intermediate type of radiation, or alternatively it may combine the properties of one of these types in one part of the spectrum with those of the other type in a different part of the spectrum.

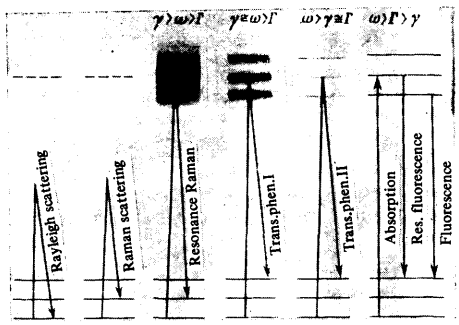


Figure 6. Optical transitions for large and for small damping (γ) of the electronic oscillator (ignoring rotational sublevels). The lower horizontal lines denote the energy of the $\overline{Ov}$ sublevels of the electronic ground state; the upper lines or bands denote the sublevels (ev) of the excited electronic level e.

The theory of Raman scattering summarised above explains [52] the ability of "quenching agents" to eliminate fluorescence with little effect on the intensity of the normally scattered light and of resonance scattering in the same material [37,49]. Normal fluorescence is due to emission from the long-lived, lower vibrational sublevels of ev (arrow labelled fl in Fig. 3), whereas resonance scattering occurs when the sublevels of ev which contribute to α_{on} have a short life-time: these sublevels are, of course, relatively unaffected by quenchers [69].

The simple quantum-mechanical theory and the Kramers–Heisenberg–Weisskopf formula do not extend to resonance scattering by a system with a non-diagonal damping matrix. The off-diagonal elements determine the relationship between the various excitation levels through the field of the radiation: they are considered in models which include quantisation of the light field [70].

IV. EXPERIMENTAL OBSERVATION OF RAMAN RESONANCE SCATTERING SPECTRA

The observation of Raman spectra usually presents no difficulty when the exciting line is not very far removed from the absorption band of the material: data are available for a large number of compounds, including nitroaniline [28,56], Michler's ketone [37,71], nitrostyrene [72], vitamin A, [37] etc. The case of excitation at a relatively large distance from the absorption band ($\nu_e - \nu > > 12\,000$ cm^{-1}) will not be considered here: it includes Harrand's experiments [73] with cinnamaldehyde, chalcone, etc.

Resonance Raman spectra have been obtained for many organic and inorganic compounds of different types and showing both continuous absorption and absorption bands with a fine structure. In addition to the experiments with potassium *p*-nitrophenate mentioned above, spectra have been obtained for solutions of other nitro and nitroso compounds [46,47,42,67,68,74,75], polyenes [11,12,76], derivatives of azobenzene and azonaphthalene [54,75,77,78], pseudoisocyanine [74], Malachite Green [37], $KMnO_4$, [79] iodine [80], and many others (see Ref. 81 for a detailed review). Spectra have also been reported for solids: nitro compounds [5,82], semiconducting crystals [83,84], *F*-centre spectra for alkali halide crystals [85], impurity ions [86], etc. [87] Specially interesting results were obtained with vapours [86]. In all cases the molar intensity of the Raman lines was very high. The largest intensity coefficient was reported for the ester ROOC–(CH=CH)$_7$–COOR: for the 1550 cm^{-1} line it had the value 400×10^6, higher than the strongest acetone line [12] by a factor of 20×10^6. Hence, the line can be observed at concentrations as low as 0.00001% (see Section XI). With lower values of γ the intensity of the secondary emission lines can be even higher (by several orders of magnitude).

Electronic transitions polarised along the chain are characteristic of molecules with an elongated system of conjugated bonds. The corresponding Cartesian component of α_{on} is overwhelmingly dominant under resonance conditions, and hence the degree of depolarisation ρ of most of the Raman lines approaches the value 0.5. [15,67,28,72,88,89] In planar, branched systems ρ can tend towards a different limit of 2/9 (see the results for benzophenone [88]).

Excitation experiments in the absorption region do not always yield positive results [68,37]: this is evidently because the intensity of the line under study includes a contribution from the electronic level, which is to some extent a function of f'_e and ν'_e. When $\nu'_e = 0$, the observation of Raman scattering in the resonance region should be difficult if not impossible, both because the intensity is lower and because of interference from fluorescence bands [27].

Re-absorption of the radiation, even in the region of the strongest absorption bands ($\epsilon > 100\,000$), does not preclude the observation of the stronger Raman lines in sufficiently dilute solutions. An optimum concentration can be defined for each compound [67,75,90]: the formula is given in Ref. 90.

Resonance Raman spectra have provided a broader understanding of the interaction of light with molecules, have led to important results on the relationship between scattering, absorption, and fluorescence spectra, have increased the technological possibilities of Raman spectroscopy, and have given a satisfactory explanation of the effect of conjugation on Raman spectra in systems with different numbers of branches. Perhaps the most interesting results are those on the intensity of resonance Raman spectral lines excited in the region of an absorption band with a developed structure, and in different parts of such a band. These experiments have confirmed the early suggestion [46] that several maxima can appear in $I(\nu)$ under conditions of this type, and also the predictions [33,29] of the life-time of the excited state of a molecule. More details will be found in Section XI.

V. CHARACTERISATION OF MOLECULAR FRAGMENTS IN THE PRESENCE AND IN THE ABSENCE OF CONJUGATION

It is conventional, in studies of intramolecular interactions, to separate the inductive effect from the effects of conjugation (see, for example, Ref. 91 and 92). This procedure, though convenient, is arbitrary to some extent. Different authors use a slightly different interpretation of the inductive effect. In what follows, the term will be used to denote the polarisation of one fragment of a molecule by the electric field produced by another fragment, without redistribution of the electron density in the intervening region.

Conjugation, on the other hand, is the interaction between the electron clouds of two or more chemical bonds. The interaction can be described by a partial *overlapping* and *combination* of their wave functions, set up on the assumption of no interaction (for example, if the conformation of the molecule is unfavourable), with the assistance of the *vacant orbitals* of the fragments. The three aspects which are italicised above differ in their relative importance towards the manifestations of conjugation in different properties of the molecule. Hence, the possibility of establishing simple general correlations is extremely remote.

There is no difference in principle between the various types of conjugation ($\pi-\pi$, $n-\pi$, $\sigma-\pi$, $\sigma-\sigma$). [92,93] They differ only in the form of the overlapping wave functions: the form specifically determines the influence of the mutual orientation of the interacting fragments upon the conjugation. Conjugation increases the number of possible electronic transitions, it has a powerful effect on the optical properties of the molecule, and it leads to a redistribution of the electron density between different groups.

The contribution of the lowest vacant orbitals of the two fragments of the X=C–C=Y system to the filled molecular orbitals is the basis of the so-called "π-electron delocalisation", which amounts to a delocalisation of the valency lines (but in no way characterises the motion of electrons). The redistribution of electron density between non-identical groups of atoms is described in terms of the preferential occupancy of the vacant orbital of one of the fragments. The extent of redistribution is affected by solvation, by the formation of transition complexes, by the application of an external field, by electronic excitation, and during vibration of the atoms. The latter is relevant to the intensity of infrared absorption bands. Depending on the frequency ω and on the extent of overlap of the orbitals of the fragments, the conditions for adiabaticity may or may not be met. The same is true of the frequency of the external field. The aspect which relates to chemical reactions is discussed in Ref. 94.

Conjugation and the redistribution of electron density, under equilibrium configuration and during atomic vibrations, have a significant effect on the frequencies and on the stiffness of chemical bonds. The inductive effect is invoked by many workers, but its role is often exaggerated (see, for example, Sections X and XI and Ref. 95, 96). It is important to note that the relative importance of the various factors which determine the intensity and the frequency of Raman lines is by no means the same: the mutual relationship is far closer in the case of optical properties such as the intensity of Raman lines, polarisability, dispersion, and u.v. absorption spectra (see Sections II and III, and Ref. 97).

The intensity of the Raman lines is one of the molecular parameters most sensitive to conjugation. The reason for this high sensitivity is the presence of higher-power terms in the resonance denominators (see Eqn. (2)). At the same time the intensity (as in the case of the u.v. spectra) is often relatively insensitive to the inductive effect (see Sections IX, X, XI, and also Ref. 95, 96, 98, and particularly Ref. 99 and 100, where reference is made to the Taft constants). When the spectrum is excited close to resonance the intensity is more clearly related to the properties of the particular excited electronic level. Far from resonance and at low field intensities the strength of the Raman lines (like the polarisability) is best described in terms of the characteristics of the electronic ground state.

When the spectra are used to gain information on particular atomic groups in complex molecules it is important to remember that entirely different conditions apply to the localisation of electronic excitation and of normal atomic vibrations. It is not hard to think of a model of the molecule such that electronic excitation is delocalised, but atomic vibration is not, and vice versa. The first case includes molecules in which the fragments involved in conjugation have very different mechanical parameters: for a vibration largely localised in one particular (i-th) bond, $\frac{\partial \alpha}{\partial Q_m} \simeq \frac{\partial \alpha}{\partial q_i}$. But even if the mechanical parameters are similar and the normal vibration can extend to both fragments, we cannot in principle exclude the possibility of

transition to a localised characteristic—from $\frac{\partial \alpha}{\partial Q_m}$ to $\frac{\partial \alpha}{\partial q_i}$ and from $\frac{\partial \nu_e}{\partial Q_m}$ to $\frac{\partial \nu_e}{\partial q_i}$. It should be noted, however, that the partial differentials with respect to q_i (with q_j = const) involve some arbitrariness in the choice of the other internal coordinates $j \neq i$. This is not surprising: the type of deformation of the molecule for a given change of q_i depends on which of the other internal coordinates remain unchanged (see Ref. 101).

As regards the separation of α and also $\frac{\partial \alpha}{\partial q_i}$ into the contributions from particular chemical bonds, which is often attempted, this approach has physical significance only if the bonds are very different, i.e. if local electronic excitation is possible. When the bonds are identical (e.g. in n-alkanes) the electronic excitation levels relate to the whole chain, as in the case of polyenes, but we can formally define the "polarisability" of individual C–C bonds; this procedure gives satisfactory numerical results only when the frequency ν_e is well removed from the frequency ν of the incident light. The increments of α (and also of α') are additive in this case because slight variations in the very high frequencies ν_e and the splitting of the energy levels for different lengths of the –C–C– chain have a negligible effect on the resonance denominators of the expressions for α and α' as compared with (for example) variations in ν_e for the closely spaced levels of polyenes. (Of course, differences in ν_e are also relatively larger in the polyene series [93].) We note that even when identical groups are very weakly conjugated they are included in equal measure in the molecular orbitals.

It should be evident from this example that additivity in the properties of complex molecules (i.e. the ability to describe molecular constants as the sum of increments proper to individual atoms or bonds) is not directly linked, in general, to the location of the actual physical phenomena in which these properties manifest themselves. The concept of delocalisation of the electronic excitation energy and of the atomic vibration energy is quite well defined if specific time constraints are assumed: we have already pointed out that the splitting of levels due to coupling between oscillators is not small, and the "measurement time" and the mean life-time of a state are quite large.

By assuming constant contributions from particular chemical bonds to α and to $\partial\alpha/\partial q$, successful predictions for different molecules can be made, and (if conjugation is absent) good results are obtained for the polarisability and for α'.[102–105] However, the differentials of the polarisability are more sensitive than is α to interactions between groups, and this sets a limit to the usefulness of the additive approach. It is a relatively useless formalism [107] to extend the scheme by taking the differentials $\partial\alpha_j/\partial q_j$ into account, as was done in an attempt to calculate the contribution of an individual bond to the exaltation of refraction [106]. Yet, the most interesting and important cases do involve non-additivity, and one must turn to the values of $\partial\alpha/\partial Q$ and $\partial\alpha/\partial q_i$, and direct measurements of Raman line intensities. Nevertheless, various workers have tried to separate the polarisability parameters of different bonds [54,108].

The possibility of describing the donor–acceptor properties of atomic groups by means of some simple coefficient is very attractive. In practice, however, these properties are strongly dependent on the specific combination of atoms in the group and on their mutual orientation. It is more profitable to consider separately two types of donor–acceptor property: 1) involving an increase and 2) involving a decrease in the multiplicity of the bond between the two interacting groups [109,110]. The OH group must be considered to be a donor group according to its donor–acceptor properties of the first type, and an acceptor group according to its properties of the second type. Depending on its angle of rotation, the amino group can be assigned either to the electron-donating groups of the first type or to the acceptors of the second type. The redistribution of the electron density between the groups depends on the difference between their donor–acceptor properties of the first kind and on the difference between their donor–acceptor properties of the second kind. Thus, every group can be characterised by two coefficients, each of which depends on the angle of rotation of the group.

The possibility of locally characterising the mechanical properties of chemical bonds, even in the absence of conjugation, is very limited. Neither the force constant K_{ii}, nor the interaction coefficient, nor the "independent force constant" (i.e. independent of the choice of the coordinate system for the molecule [101]) can give an accurate characterisation of an individual chemical bond. Strictly speaking, the i-th bond can be characterised only by a set of coefficients (for example, the K_{ij} matrix) which includes off-diagonal coefficients [111,112]. Among these, the most interesting and important are those which describe the interaction of neighbouring chemical bonds: even in paraffin hydrocarbons these coefficients do not vanish [112]. Conjugated double bonds also can interact very significantly [112–115]. All these effects stem from the dependence of the contributions to the inductive effect upon the nuclear coordinate, from the influence of atoms which are not chemically bound, and from conjugation and its associated redistribution of the electron density between the bonds [101]. The off-diagonal coefficients K_{ij} as a rule are much smaller than K_{ii}, but their differences can be as important as the differences in K_{ii} when molecules with different amounts of conjugation are compared. Examples may be quoted ($\omega_{C=O}$ in succinimide, succinic anhydride, etc.) where the difference in frequency between two stretching vibrations is determined mainly by the K_{ij} coefficients. Some data on the relationship between K_{ii}, the order of the chemical bond, and the interatomic distances can be found in the literature [113,116,117].

The classification of molecules into those which do and those which do not show additive behaviour can lead to entirely different results when different properties are studied, and it can depend on the choice of the internal coordinate system for the molecule [111]. Distinguishing between multielectronic and monoelectronic properties of molecules (Dewar [91]) is a somewhat indefinite approach, lacking a concrete physical basis. We prefer to consider the connection between the parameters and electronic excited levels, and also the "time factors" ("measurement time", etc.).

VI. MEASUREMENT OF RAMAN LINE INTENSITIES. SYMBOLS

The intensities of the Raman lines of different compounds are usually determined by reference to the line intensity of a standard compound. The scale which was first proposed took the 313 cm^{-1} line of liquid CCl_4 as 100 units; the intensity of the unknown line was obtained for equimolar proportions of the compound and CCl_4. [17]‡

‡A different scale, in which intensities are referred to unit volume, has been proposed by Sushchinskii [27].

For analytical purposes, the maximum intensity of the line is measured in a spectrometer with a narrow slit, whereas in structural studies the integral intensity is measured [15,28].

The spectra of the unknown and of CCl_4 can be measured separately, under identical conditions (external standard method), or alternatively one can measure the spectrum of a solution in CCl_4 or in another solvent (internal standard method). [117,118] The advantage of the second method is that the results are relatively unaffected by the refractive index of the liquid, which determines the path of the light rays in the cell, and also by light absorption, temperature, stability of the light source, and the specific properties of the medium containing the molecules under study. These advantages are quite important, because reliable corrections for all these factors have not yet been worked out. In practice, of course, most materials are solids of low vapour pressure, and have to be studied in solution irrespectively of the advantages of the two methods, since direct measurements of line intensities on solid samples are not very accurate.

In order to minimise the angular dependence of the intensity, the usual cylindrical cell for the sample is sometimes fitted with a screen which polarises the light at right angles to the cell axis [119]. Under these conditions, the contribution to the intensity from the anisotropic part of the scattering tensor becomes smaller: the term $45\bar{\alpha}'^2 + 13b'^2$ of formula (1) is replaced by $45\bar{\alpha}'^2 + 7b'^2$, and we have the relation [25,120]

$$45\bar{\alpha}'^2 + 13b'^2 = (1+\rho)(45\bar{\alpha}'^2 + 7b'^2) = \frac{6(1+\rho)}{6-7\rho} \cdot 45\bar{\alpha}'^2.$$

However, equally good results are obtained by using simple diaphragms to limit the range of angles of incidence to 90–15°: with this precaution, no modification of formula (1) is necessary. Corrections for self-absorption in the sample can be applied [37,121,122]; other corrections have been discussed in recent monographs [25,27].

The spectra of vapours are very important means of characterising molecules, but they are very difficult to obtain in most cases, and solution spectra have to be examined instead. Under these conditions, the Raman lines of the solvent can be used as internal intensity standards.

For the most accurate measurements of intensity and frequency over a range of materials it is convenient to use a single, well characterised, and preferably inert solvent. Cyclohexane could be quite useful but for its limited solvent power. Solvent effects on the frequencies of various groups in organic compounds have been reported [19,123,124]; these effects have been used in assigning lines [125,126].

In mixtures of aliphatic hydrocarbons, and in a number of other systems, the molar intensity coefficient is independent of concentration [24,67,75], but a significant concentration dependence is found in many cases (in particular, when the degree of association is a function of concentration).

The intensity of lines from the solute usually increases with the refractive index of the solution, even when a correction for convergence of the beam in the cell is applied. On varying the refractive index of the solvent over the range 1.25–1.60 the intensity coefficient for non-resonance excitation is found [132,133] to vary by ±40%. Various approximate formulae for non-specific intermolecular interactions, based on the Onsager model, are derived by Wahl [132]. Association and complex formation introduce additional complications [134–136].

The influence of solvent type is more marked under near-resonance conditions, when the relationship between the shift in the u.v. absorption band and the intensity change becomes unmistakable [15,33,49] (see formula (2); see also Ref. 66, 67, 136–139).

In gases, the line intensity increases with temperature as predicted by theory. In the liquid phase at room temperature the intensity is higher than in the gas phase by a factor of 1.5–3, but on raising the temperature the difference decreases [140]. Most measurements are made at 20–30°: more accurate temperature control is seldom needed in practice.

An attempt has been made to define line intensity constants which are less dependent on measurement conditions: one of these is the absolute intensity [143], or the "activity coefficient" for scattering [144] to use the more recent terminology:

$$A = q_i(45\bar{\alpha}_i'^2 + 7b_i'^2),$$

where q_i is the degeneracy of the nuclear vibrations; in this formula the normal coordinates have the dimensions cm $g^{1/2}$, and the "activity coefficients" are in $cm^4\ g^{-1}$. The latter can be evaluated from experimental data by eliminating the factors $(\nu-\omega_m)^4$ and $[1 - \exp(-\frac{h\omega_m}{kT})]$ and multiplying by ω_m (see formula (1)). The line of the rotational Raman spectrum of the hydrogen molecule ($J = 1 \rightarrow 3$), which has been reliably characterised, has been proposed [145] as a standard for the experimental determination of A. The following results have been obtained: for gaseous CCl_4 $A_{459} = 13.2 \times 10^{-8}$, [146–149] $A_{313} = 4.3 \times 10^{-8}$, [147] whilst for liquid CCl_4 [140,149] $A_{459} = 34 \times 10^{-8}$, $A_{313} = 10.1 \times 10^{-8}\ cm^4\ g^{-1}$. The ratio of the A values for the measured line and for the 459 cm^{-1} line of CCl_4, $S = A_X/A_{459}$, is called [119] the "standard intensity".

The use of coefficients with dimensions $cm^4\ g^{-1}$ ("absolute intensity") to characterise the line intensity has no particular advantage, and introduces unnecessary complications into the interpretation of experimentally observed quantities. Both from the physical and the chemical points of view, it is quite satisfactory to retain the conventional (relative) intensity coefficients, the differentials of the polarisability, or the polarisability matrix elements α_{0n}. For non-resonance excitation the quantity $2\alpha_{01}$ can be identified with the difference between the polarisabilities at the two extreme positions of the nuclei. For a discussion of the "scattering cross-section" the reader is referred to the literature [22,27,150,151].

In the remainder of this review, molar integral intensity coefficients for room temperature are discussed in the text and listed in the Tables. The intensity of the 313 cm^{-1} line of liquid carbon tetrachloride excited by non-polarised light (λ = 4358 Å), and observed at a scattering angle of about 90°, is taken as 100 units; intensity coefficients referred to this standard are denoted by the symbol I^S. The same standard can be used for excitation by frequencies < 22 938 cm^{-1}. The precision of the intensity measurements varies from ±5 to ±20%, depending on the type of apparatus used.

The following I^S values have been reported for liquids: 109 for the 459 cm^{-1} line of CCl_4, [103,118,140,152–157] 43.5 for the 802 line of cyclohexane, [103,158–161] 24 for the 1176 line of benzene [24,28], 12 for the 1031 line of methanol [37,158]; the results are practically identical whether the measurements are made on the pure liquids or on solutions in CCl_4. Excitation by light of much longer wavelength has very little influence on the relative intensity of these lines.

Measurements with a He–Ne laser have also been reported[141,142].

The following symbols are used throughout the remaining Sections: R, Et, Ph for the methyl, ethyl, and phenyl group respectively, Π for a π-bond or a π-bond system. H atoms attached to carbon are omitted in the structural formulae. Q is the normal nuclear coordinate, q is the elongation of the interatomic distance (natural coordinate) in cm or Å.

VII. INTENSITY OF THE RAMAN LINES OF SIMPLE MOLECULES

The differentials $\partial\alpha/\partial q$ (Table 1) are specially interesting as a link between the intensity of Raman lines and other physical constants of the molecule. The best results, obtained for diatomic molecules, justify a number of generalisations about the relationship between line intensity and the nature of the chemical bond. Values of $\partial\alpha/\partial q$ have been obtained also (for relatively simple molecules) by assuming additivity: these need to be interpreted with greater care. The values listed in Table 2 relate to solutions in CCl_4 or to the pure liquids (except for the values for ions, which relate to aqueous solutions). Numbers in brackets are estimates made by analogy or from u. v. spectral data. Values for some other simple molecules and ions can be found in the literature[179,182,187,188]. Force constant data are tabulated by Müller and Krebs[181].

Table 1. Raman spectra of gases.

Molecule	ω, cm^{-1}	I^s	$\partial\alpha/\partial q$, Å^2	References
H_2	4160	14	1.25	144, 145, 162, 163
D_2	2993	12	1.22	145, 162
N_2	2330	6.5	1.7	162–164
O_2	1555	10	1.45	162–164
HCl	2886	—	1.0	164
HBr	2558	—	1.2	164
CO	2155	6.5	1.5	162, 163
$H_3C{-}CH_3$	994	—	1.0	165–168
$H_2C{=}CH_2$	1623	~12	1.9	165, 166, 169
$HC{\equiv}CH$	1973	35	3.15	165, 166, 168
CO_2	~1340	19	1.95	162–164, 169, 170
CH_4	2914	32	1.05	147, 166, 168
CD_4	2108	25	1.0	167, 171
CT_4	1738	(22)	1.0	167
CR_4	734	20	1.15	166, 172, 173
CF_4	908	7	0.97	147, 171, 173
CCl_4	459	42	2.1	147, 168, 174
SiR_4	596	~65	~1.9	172
SiF_4	800	7	0.88	171
GeR_4	559	~100	~2.2	172
SnR_4	507	~200	~3.0	172, 176
PbR_4	459	~300	~3.2	172, 176
NH_3	3334	~ 20	~1.0	162
H_2S	2614	32	~1.3	162
SF_6	775	20	1.23	171
SeF_6	710	32	1.47	171
TeF_6	697	31	1.4	171
AlkOH	3640	~7	1.0	132, 175, 177

It has been known for many years[22] that purely ionic bonds cannot contribute to Raman scattering, because the electron clouds of the cation and the anion are mutually independent. (Ion pairs in close contact can give very weak lines.) Bonds with a weakly covalent character give low-intensity lines because[189] the potential energy curve of the excited electronic level has a small curvature. In the simplest cases, this small curvature can be ascribed to the fact that the energy difference between the bonding and the antibonding molecular orbital is relatively unaffected by bond stretching, since it is due to a difference in the field surrounding the two atoms rather than to overlapping atomic orbitals.

Table 2. Raman spectra of compounds in the liquid phase (column headings as in Table 1).

Molecule	ω, cm^{-1}	I^s	$\partial\alpha/\partial q$, Å^2	References
CCl_4	313	100	—	—
	459	109	3.35	see Section VI
CBr_4	267	360	6.0	178, 179
CI_4	178	(2000)	—	180, 181
$SiCl_4$	424	130	3.3	130, 178, 182
$GeCl_4$	396	290	4.8	130, 178, 182, 183
$SnCl_4$	367	540	6.1	178, 179, 182, 184
$SnBr_4$	221	1540	10.6	184, 178
SnI_4	149	(20000)	(~35)	180
$TiCl_4$	387	920	8.4	178, 182
PCl_3	510	170	—	182
PCl_5	394	800	—	182
$SbCl_3$	360	450	—	182
$BiCl_3$	288	520	—	182
$ZnCl_4''$	282	40	1.45	179
$ZnBr_4''$	172	170	3.0	179
$HgCl_4''$	267	260	3.5	179
$HgBr_4''$	166	1500	8.5	179
CO_3''	1060	21	1.75	182, 185
NO_3'	1040	62	2.8	182, 185
PO_4'''	935	22	1.55	182, 185
AsO_4'''	820	70	2.35	182
SO_4''	980	45	2.3	182, 185
ClO_3'	934	50	2.3	185
ClO_4'	935	73	2.9	185
IO_4'	797	226	4.6	185
$(N{=}N{=}N)'$	1343	47	—	186
CN'	2079	18	2.9	187

$\partial\alpha/\partial q_i$ is practically unaffected by isotopic substitution. The intensity can vary a little because of the difference in the amplitudes q_i, but this effect is negligible except in the case of the hydrogen isotopes. The intensity and $\partial\alpha/\partial q$ both increase with the multiplicity of the bond; for carbon–carbon bonds $\partial\alpha/\partial q$ is proportional to the order of the bond[166]. For C–H bonds (but not for C–C bonds[187]) $\partial\alpha/\partial q$ is independent of hybridisation of the atomic orbitals of the C atoms[132,166]. The intensity of the lines of MX_n molecules increases very considerably[182] as the valency of the M atom increases. Differences in $\partial\alpha/\partial q$ for chemical bonds of a given type in molecules and ions are generally small; no obvious trend has yet been detected. The intensity and $\partial\alpha/\partial q$ increase with the atomic weight of the atoms involved in bond formation: if σ-bonds are compared, this effect may be explained by the decrease in the energy of the $\sigma \rightarrow \sigma^*$ electronic excitation.

Some of the above aspects are implicit in the approximate empirical formula for MX_4 molecules given by Pauling for $\partial\alpha/\partial q$ in terms of the percentage covalency (p) of the bond, defined by the electronegativity difference between M and X:

$$\partial\alpha/\partial q \sim p(z_M + z_X),$$

where z is the atomic number of the element[178].

Lippincott [190] gives a relationship between the differential $\partial\alpha/\partial q$ and the multiplicity (n) of the bond, the electronegativity of the atoms in the given valency state (χ_1 and χ_2), and the number of filled s, p, d, and f shells. In his model, the potential in the region of each nucleus is described by a δ-function. A local molecular orbital independent of other bonds is obtained by a linear combination of the wave functions of the two atomic orbitals. In Long and Plane's interpretation [179], this model gives the differential of the bond polarisability in the form

$$\frac{\partial\bar{\alpha}}{\partial q} = \frac{\sqrt[4]{\chi_1\chi_2}}{\sqrt{z_1 z_2}} \frac{\sigma n q_0^3}{a_0};$$

where $\sigma = \exp[-\frac{1}{4}(\chi_1 - \chi_2)^2]$ defines the covalent character of the bond, q_0 is the equilibrium distance between the atoms, a_0 is the Bohr radius of the first orbital of the H atom, and z is the effective charge on the nucleus. Lippincott and Nagarajan [190] replace z by empirical functions of the filling of the s, p, d, and f shells; values of x/z are tabulated for all atoms [191]. This formula often leads to serious discrepancies with experiment. It has been used [179] to evaluate bond multiplicity in a large number of molecules and ions.

Non-empirical and semi-empirical quantum-mechanical methods have been used a number of times to calculate $\partial\alpha/\partial q$ for the hydrogen molecule: in general, the results were satisfactory [325]. Further discussion of the application of the additivity hypothesis to polyatomic molecules can be found in Ref. 173, 189, 192–194.

VIII. INTENSITY OF THE CHARACTERISTIC LINES OF THE MOST IMPORTANT ATOMIC GROUPS

Among the most interesting Raman lines of organic compounds are those which characterise the quasi-local stretching vibrations of atomic groups (for example, carbonyl, hydroxyl, cyano, nitro). Their position in the spectrum (Table 3) is relatively independent of the structure of the rest of the molecule. In the few cases where such a relationship was observed, it was ascribed to the effect of conjugation or some other form of intramolecular interaction upon the rigidity of the chemical bond.

The intensity of the Raman lines for quasi-local vibrations usually varies very little among the members of a homologous series. Thus, in the alk-1-ene series from pentene to tetradecene (and also in the cycloolefins [197,276]) the intensity of the so-called "C=C vibration" line lies between 30 and 35 units; similar information exists for other hydrocarbons [24,161,198]. Replacement of the H atoms on the C=C double bond by alkyl groups increases $I_{C=C}$ (to 50 in the case of tetraalkylethylenes); [195,198] calculations by the additive scheme suggest that this effect may arise from the contribution of the new bonds to the differential $\partial\alpha/\partial Q$, without any change in the parameters of the double bond ($\partial\alpha/\partial Q_{C=C}$). [105] It should be noted, however, that the u. v. absorption bands of alk-1-enes and tetramethylethylene appear in different positions, and this effect alone may explain an increase in intensity by 25–30%; thus, the simple "additivity scheme" is not fully adequate in this case. A similar state of affairs is found on going from toluene to hexamethylbenzene (line at ~ 1600 cm^{-1}). [199] A small increase in $I_{C=O}$ and $I_{C\equiv N}$ is observed experimentally when comparing the first with the subsequent members of the ketone [100,200,201] and the cyanide [99,138] homologous series.

Various workers [98,35,202–209] have reported an approximate proportionality between characteristic line intensities and the number of like atomic groups when the latter are separated by one or more carbon atoms with sp^3 hybridisation, or by the group SiR_2 or SnR_2§. Molecules with different bridging groups often show significant deviations from additivity (see Section XIV).

Table 3.

Group X chemical bonds		Alk—X ω	Alk—X I^S	Alk—X $\partial\alpha/\partial q$	Ph—X ω	Ph—X I^S	I^S(PhX)/I^S(AlkX)	References
—CH_3		~2900	~40	1.4	~2900	50	~1.2	24, 167
	C—C	~1000	—	1.2	—	—	—	166–168
—SiR_2H	Si—H	2118	90	2.1	2122	105	1.2	132, 211, 212, 326
—SH	S—H	2586	52	2.0	2586	75	1.4	132, 213, 214
—CH_2·S·CH_2—	C—S—C	680	50	—	—	—	—	214
—CH_2F	C—F	875	15	1.2	—	—	—	
—CH_2Cl	C—Cl	655	50	2.5	—	—	—	215–217
—CH_2Br	C—Br	557	100	4	—	—	—	215, 216
—CH_2I	C—I	497	200	7	—	—	—	215, 216
—CH<		~1300	26	—	1300	39	1.5	218
—CH_2—SnR_3		507	~350	—	480+ +510	~1000	~3	176, 202
—SOR	S=O	1048	48	—	—	—	—	§ 142 [sic]
—SO_2R		1135	~100	—	1160	~80	~0.8	219
—$CONR_2$	C=O	1655	21	—	1636	60	3	98, 100, 126, 220–222
—COOEt	C=O	1745	14	—	1725	100	7	15, 98, 100, 220, 223
—COR	C=O	1719	14	2.2	1690	160	11	15, 37, 98, 104, 220
—COCl	C=O	1803	12	2.5	1770	170	14	35, 100, 104, 200, 220
—COBr	C=O	1812	14	—	1780	200	14	200, 220
—COH	C=O	1729	13	2.9	1704	230	18	35, 98, 100, 104, 220
—Ph	C=C	1605	26	2.2	1600	~700	~13	107, 220, 224
—$CH=CH_2$	C=C	1642	30	3	1631	340	11	15, 37, 196, 225–227
—C≡CH	C≡C	2118	75	5	2110	400	5,3	37, 99, 129, 228–230
—CN	C≡N	2254	32	4.2	2231	330	10	35, 138, 187, 231–234
—NO_2		1380	35	—	1348	700	20	28, 35, 72, 235

Table 3 lists relative intensity data for the characteristic stretching vibration lines of various atomic groups in molecules of the RX type (mostly, EtX), and also the corresponding $\partial\alpha/\partial q$ differentials; the frequency ω is obtained from data for solutions in CCl_4 (except the starred values, which relate to different solvents); the values of I^S and $\partial\alpha/\partial q$ refer to the pure liquids or to solutions in CCl_4. We note that α' and I^S increase with the multiplicity of the bond, with the atomic weight of the bond-forming atom in X, and also with the intensity of the u. v. absorption band of RX and with its approach towards the visible end of the u.v. spectrum.

The reader is referred to the original literature for an account of the characteristic lines of various types of branched hydrocarbon chain and of cyclic molecules [27,205,208–210].

§The total intensity of the line splitting components should give a more exact proportionality.

IX. EFFECT OF SUBSTITUENTS ON THE SPECTRA OF COMPOUNDS WITH C–C π-BOND SYSTEMS

A large amount of data is available on the effect of various substituents on $I_{C=C}$ and on the differentials $\partial\alpha/\partial q_{C=C}$,[15,16,207,220,226,227,236] on $I_{C\equiv N}$,[99,138,187,235] on $I_{C=O}$,[15,98,100,200,220] and on $I_{C\equiv C}$.[99,203,204,228,230] Among these substituents, the phenyl group has attracted particular interest (see last three columns of Table 3). Table 4, on the other hand, gives some indication of the influence of other groups upon the benzene ring. It was pointed out in 1953 [71] that substituents usually have a stronger influence on the intensity of lines for conjugated bonds than on the intensity of lines for isolated multiple bonds. These relationships are discussed in Section X.

Table 4.

Group X in PhX	I^s_{1600}	EMR, cm^3	u.v.spectra in heptane λ_1	λ_2	λ_3	σ_{para}	References
—H	35	0	2540 *0.2*	2030 *7.5*	1830 *50*	0	107, 24
—D	35	0	——	——	——	0	107
—SO_2R	28	——	2640 *1.0*	2150 *8.0*	1890 *57*	0.8	107, 223
—F	28	—0.05	2600 *1.1*	2030 *7.3*	1820 *48*	0	107
—OCOR	36	——	2650 *0.3*	2100 *8.0*	1860 *53*	——	71, 98, 222, 226
—Cl	35	0.15	2610 *0.3*	2140 *8.0*	1890 *61*	0.2	107, 224
—Br	37	0.10	2610 *0.3*	2150 *8.0*	1925 *35*	0.2	107, 224
—OH	38	0.28	2700 *2.0*	2110 *6.5*	1890 *56*	—0.3	107, 153, 224
—R	39	0.25	2620 *0.3*	2050 *8.0*	1880 *53*	—0.15	17, 37, 24, 220
—NR_2H^+	~40	——	——	——	——	——	237
—CH_2CN	40	——	2570 *0.2*	2060 *7.0*	——	0	232
—C—C—Ph	40	——	2600 *0.5*	2080 *20*	1880 *100*	—0.1	220
—C—NR_2	41	——	2580 *0.2*	2070 *12*	1880 *60*	——	220
—I	42	0.15	2600 *0.7*	2300 *12.5*	1940 *28*	0.3	107, 224
—SiR_3	45	0.1	2580 *0.3*	2130 *9.0*	1900 *70*	——	238
—OR	50	0.35	2715 *2.0*	2165 8.5	1920 *50*	0.25	153, 220, 222
—O—C=C	58	——	2720 *1.2*	——	——	——	15, 223, 225, 239
	65	——	——	——	——	——	240, 241
—C—SiR_3	80	0.5	2680 *0.4*	2240 *8.5*	1950 *52*	——	238
—$B(OBu)_2$	80	——	2670 *0.8*	2200 *10.6*	1910 *47*	——	242
—NEt—COR	80	——	—— ——	2380 *5.5*	2000 *20*	——	126
—CCl_3	80	0.35	2690 *0.6*	2250 *7.0*	1925 *43*	0.45	71
—SH	90	0.5	2760 *0.7*	2350 *8.5*	2030 *22*	0.45	107, 213, 214
	90	0.3	2640 *0.5*	2190 *8.6*	1930 *52*	—0.1	218, 223, 241, 243
	95	——	2600 *0.2*	2170 *8.0*	1900 *32*	—0.1	218
—SR	100	0.8	2800 *1.5*	2540 *9.8*	2030 *14*	0	107, 223
—NH_2	100	0.95	2850 *1.6*	2350 *8.0*	1980 *30*	—0.5	34, 153, 220, 224
—CH_2I	110	——	2720 *2.2*	2340 *10*	2020 *23*	——	232
—$CONR_2$	110	——	2700 *0.6*	2250 *10*	1890 *35*	——	98, 220, 222
	112	0.45	2750 *1.0*	2340 *12*	1990 *30*	—0.3	218
—COOEt	135	0.8	2770 *1.0*	2290 *12*	——	0.6	98, 222
—CN	150	1.0	2700 *0.65*	2230 *13*	1920 *52*	0.8	34, 37, 153, 222
—NR_2	170	1.5	2960 *2.0*	2500 *14*	2010 *22*	—0.6	107, 218, 220, 224
—C≡C	180	1.4	2750 *0.4*	2380 *16*	1990 *33*	—	37, 228, 229
—COR	190	0.9	2800 *1.0*	2385 *13*	1980 *31*	0.7	37, 98, 153, 220
—NO_2	200	0.9	2810 *1.5*	2520 *9*	1980 *18*	1.0	45, 37, 107, 224
—CHO	200	1.1	2810 *1.3*	2410 *14*	1980 *27*	0.8	98, 107, 222
—NHCHO	210	——	2780 *1.4*	2390 *13.5*	1980 *24*	0	107, 126
—C=C	250	1.4	2820 *0.75*	2460 *14*	2040 *23*	0	45, 37, 224–226
—COCl	250	——	——	——	——	——	98, 222
—COBr	300	——	——	——	——	——	98
—NH·Ph	350	——	——	2830 *20*	2070 *21*	—	220, 224
—Ph	370	2.0	——	2470 *18*	2000 *38*	0	37, 107, 220, 224
—C—HgI	(1000)	——	——	2590 *16*	1990 *30*		244
—C=C—C=C	1100	3.0	——	2750 *26*	2200 *12*		107
—C=C—PCl_2	~1300	——	——	——	——		226
—C=C—COOEt	1400	3.1	——	2720 *21*	2160 *17*		107
—C=C—CHO	1800	3.3	——	2790 *25*	2200 *13*		37, 107
—C=C—NO_2	3200	4.0	——	3000 *17*	2290 *10*		107
—$(C=C)_2$—COR	(5000)	(5)	——	3100 *33*	2350 *8*		

Note. H atoms attached to carbon have been omitted in the formulae. The symbols are defined in Section VI.

Very similar mutual effects are observed in PhX compounds and in compounds with various CC π-bond systems (or one such bond) in place of the Ph group. Hence, many of the conclusions obtained from studies of PhX compounds are capable (in principle) of being generalised. However, compounds in which the π-bond system has degenerate donor–acceptor properties exhibit some additional specific features.

Table 4 lists some intensity coefficients for the characteristic line of the benzene ring, lying in the region 1570–1610 cm^{-1}. Alkylbenzenes have two closely spaced lines (the vibration modes are given in Fig. 1 of Ref. 107). The higher-frequency line is associated with a symmetric vibration of the ring (though some workers have erroneously assigned it to an antisymmetric vibration). Its intensity (but not its frequency) is extremely sensitive to the effect of substituents [125,153]. In the presence of conjugation this line is the predominant one, and the second line of the doublet makes a negligible contribution to the experimentally observed total intensity (designated I_{1600} in the Table). The spectra of PhX contain also a characteristic line at ~ 1000 cm^{-1}, whose intensity is far less sensitive to the nature of X: the ratio I_{1600}/I_{1000} can therefore be used to study conjugation with the benzene ring [153]. Table 4 gives only the I_{1600} values; for molecules containing two benzene rings the quoted value is $0.5 \cdot I_{1600}$.

The third column of Table 4 lists the exaltation of molecular refraction (EMR) for λ = 5893 Å arising from the interaction [107] between Ph and X. The next three columns give the wave lengths of the u. v. absorption band maxima which are genetically related to the benzene bands (λ given in Å for solutions in heptane). The figures in italics are $\epsilon/1000$ values, where ϵ is the molar decimal absorption coefficient at the band maximum [244]. The penultimate column contains the Hammett σ_{para} constants. Literature references to the quoted I_{1600} values are given in the last column of Table 4.

Table 4 summarises the properties of compounds with different types of substituent X. No direct effect on the spectrum is observed, whether the group is an electron donor, an electron acceptor, or neutral, and also whether or not it contains multiple bonds, unshared electron pairs, or heavy atoms. In each of this types, both "active" and "inactive" groups can be found. There is only one important general rule: large values of I_{1600} and EMR are usually associated with u. v. absorption bands which are both strong and close to the visible region of the spectrum. As a rule, substituents of all types tend to increase λ, I_{1600}, and EMR. [107,244] However, the deviations from additivity of the dipole moments (Δμ, see Ref. 107) are not all of the same sign: hence some justification exists for classifying substituents into electropositive and electronegative types.

When the substituent X in PhX compounds contains CC π-bond systems, both Δμ and σ are almost zero, and yet the deviations from additivity in the optical properties are large. On the other hand, substituents which favour the inductive effect (F, NR_2H^+, SO_2R) have finite (and often large) values of σ and Δμ, but their effect on the optical properties is very slight. Cases have been reported of substituents affecting some optical properties in the positive sense and others in the negative sense. Hence we may conclude that simple (linear) correlations between the optical parameters, the electronegativity of the groups X, and the σ constants are unlikely to exist [107] (see also Sections V and XII).

It is evident, from the general properties of PhX compounds, that the intensity of the Raman lines due to

π-bonds is extremely sensitive to conjugation ($\pi-\pi$, $n-\pi$, $\sigma-\pi$) and relatively insensitive to the inductive effect. Donor–acceptor interactions (leading to a redistribution of the electron density between parts of the molecule), to which anomalies in the dipole moment are ascribed, have only an indirect influence on the optical properties.

A consideration of the system of energy levels or MO energies for models of the type PhX or C=C–X makes it obvious that the absorption bands can be shifted towards longer waves by electronegative, electropositive, or even neutral X substituents in the presence of conjugation [244]. The potential well model of the electron indicates that the electronic levels should move closer together when the well is made wider. Thus, any addition to the molecule which increases the length of the chain (at least, in the absence of steric hindrance) should induce a bathochromic shift of the u. v. absorption bands [93] and increase the intensity of the Raman lines.

Table 5. Spectroscopic evidence for the effect of substituents X (shown above the numerical entries) in compounds of type PhX (I_{1600}, figures on the left) and C=C–C—X ($I_{C=C}$, figures on the right); the differences in $\omega_{C=C}$ between the compounds C=C–C–X and C=C–Alk are shown in heavy type.

I	II	III	IV	V	VI	VII
Li (50) (>1000) — —		 (100) 35 **–7**	CR_3 39 30 **0**	NR_2 170 30 **0**	OR 50 (30) **–2**	F 27 (25) **8**
Na — — — — **~–100**	MgAll — — — — **–40**	$AlAll_2$ — — — — **–12**	SiR_3 40 54 **–12**	PR_2 (80) — — **–7**	SR 100 (40) **–5**	Cl 35 35 **0**
	ZnAll — — — — **–20**		GeR_3 (40) 100 **–12**	AsR_2 (60) (100) **–10**	SeR (100) (70) — —	Br 37 55 **–5**
			SnR_3 (50) 260 **–17**	$SbAll_2$ — — — — **–13**	TeAll — — — — **~–10**	I 42 90 **–14**
	HgCl — — 700 **–15**					

Note. Numbers in brackets are tentative estimates of I from u.v. spectral data. "All" denotes the allyl group. This Table was assembled from data in Refs. 232, 245, 246, and also 176.

We shall now consider in detail the influence of substituents not containing multiple bonds. Table 5 gives some indication, in spite of the scarcity of experimental data, of the way in which the position of the substituent atom Z in the Periodic Table affects its influence on a π-bond or a π-bond system (denoted by the letter П) in groupings such as П–Z and П–CH_2–Z.

When Z is directly adjacent to П, the largest effect on the optical properties and on the rigidity of the bonds is produced by the atoms N and S ($n-\pi$ conjugation). The P atom has a significant effect, and its orbitals (including $3d$) contribute to the delocalised MO [226] (see also Ref. 227). The influence of the boron atom is ascribed [242] to the contribution from its vacant $2p$ orbital.

There is a shortage of data on the influence of Z on the force constants (rigidity) of π-bonds in П–Z systems, and indirect arguments are unreliable in this context, because of the appreciable contribution from the C–Z bond to the "π-bond vibration". Increased rigidity in П–Z systems (as compared with П–R systems) has been observed on a number of occasions (fluoro derivatives, chloro-anhydrides); decreased rigidity of C=C, C≡N, C≡C has been found to be induced by the atoms Si, Ge, Sn, [207] O, [247], S, [225,247] and N. [248] The effect of the Si, Ge, and Sn atoms arises mainly from $\pi-d$ conjugation involving the vacant d orbital of the Z atoms, [204,207,249] or from the inductive effect [207,250]; the effect of halogens is mainly inductive [200], that of the N, S, and O atoms is the result of $n-\pi$ conjugation.

Compounds in which Z is from Groups I–III of the Periodic Table have not been investigated in detail, but a significant lowering of the frequency of multiple bonds has been observed (see for example Ref. 251). This effect may be partly due to a decrease in the rigidity of the bond. However, calculated values of $K_{C\equiv N}$ for RHgCN and $Hg(CN)_2$ did not differ appreciably from those for RCN. [252]

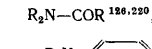
Decreased rigidity of a π-bond is often accompanied by an increased intensity of the Raman line. In spite of the contribution of the ordinary C–Z bond to the "π-bond vibration" of the П–Z system in antiphase (provided the mass of Z is not too low), [225] the intensity of the π-bond line is usually increased by substituents [204]. This is closely bound up with the fact that conjugation in its various forms tends to shift the u. v. bands towards the longer-wave end of the spectrum (see above). According to Jones [253], the values of I^{S}_{CN} for mercuric cyanide and $H_2C(CN)_2$ are practically identical.

X. $n-\pi$ CONJUGATION

The influence of atoms having a labile unshared electron pair on the rigidity of π-bonds and on the optical properties of the compound is usually ascribed to $n-\pi$ conjugation involving a π^* orbital, but some workers have invoked the inductive effect [248]. The rigidity of the π-bond is decreased by a small amount (3–5%), and the rigidity of the C–Z bond is increased by a large amount (up to 30%): [248] this is usually interpreted as some measure of double bond character. It is interesting to note [248] that the off-diagonal force coefficient which determines the interaction between the C–Z and the π-bond has a positive influence in this case: this means that stretching of the π-bond is accompanied by a shortening of the C–Z bond and vice versa [101].

The tendency of the Z atom to $n-\pi$ conjugation depends [254] on the p character of the orbitals of the unshared pair: the most favourable conditions correspond to overlapping of the n and π orbitals in П–N< systems.

Compounds with a well developed $n-\pi$ conjugation show a bathochromic shift of the u. v. absorption bands and an increased intensity of the Raman lines for the multiple bond. Some of these systems are listed below in increasing order of effect of $n-\pi$ conjugation on intensity:

AlkO—COR [15,220], AlkO—C≡C [15,226,239,255],
AlkS—C≡C [225],
R_2N—COR [126,220], R_2N—C≡N [138], Alk_2N—C≡C [126],
R_2N——COR [219], R_2N——NO_2 [46].

There is no increase in the intensity of the C=O line for the first member of this series, but in the last two

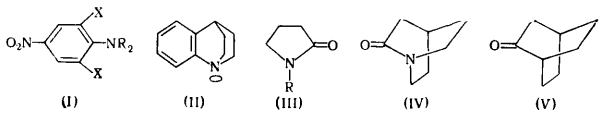
members I_{CO} and I_{NO_2} are increased by over a factor of ten as a result of the presence of the amino group. The fact that the amino group increases I_{CO} by only a factor of 1.5 in R_2NCOR and by a much greater amount in *p*-aminoacetophenone is explained by the relative positions of the strong u. v. absorption bands of these compounds (in the far u. v. for the former, and much nearer the visible region for the latter). The shift of a closely spaced band is reflected more strongly by the resonance denominator in the expression for the intensity than is the shift of a more remote band. (We note, however, that the λ shift produced by an amino group becomes somewhat smaller when the chain of conjugated bonds is extended still further.)

The redistribution of electron density between substituents, which affects the dipole moment of the molecule and $\omega_{C=O}$, is determined by different considerations. The effect is strongest if R_2N and COR are immediately adjacent, somewhat weaker if these two groups are separated by a benzene ring, and weaker still when a more complex system of CC π-bonds is interposed. These observations are easily explained by considering the systems of energy levels of the main fragments of the molecule and the combination of their wave functions with formation of delocalised MO and new electronic transitions (see, for example, Fig. 6 in Ref. 244).

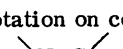
In the light of the above, it is not surprising that the anomalies in optical properties of the molecule $PhCONR_2$ are associated mainly with interactions in the Ph–CO system, whereas the dipole moment anomalies relate to the system $CONR_2$.[220]

On spectral and dipole moment evidence[219,231] conjugation with the SO_2 group is very weak in sulphonamides; the observed shortening of the N–S bond is ascribed[256] to local interaction with the vacant S *d*-orbital.

The $n-\pi$ conjugation conditions are very dependent on the angle of rotation of the conjugated groups. In unsubstituted dimethylaniline, when steric hindrance is negligible, the two methyl groups are symmetrically disposed on one side of the plane of the benzene ring, and the wave function of the unshared pair of electrons effectively overlaps the *p* orbital of the carbon atom. The same is true of 4-nitrodimethylaniline. In the 2,6-disubstituted derivatives of dimethylaniline and 4-nitrodimethylaniline (I), the NR_2 group is rotated through an angle which does not favour conjugation (the direction R...R forms a fairly large angle with the plane of the ring). The influence of NR_2 on the benzene ring and on the nitro group becomes much weaker[257]. In benzoquinuclidine (II) the wave function of the unshared electron pair (shown by an oval symbol in formula (II)) is "cleaved" by the nodal plane of the *p* orbitals of the ring into two equivalent zones: the $n-\pi$ overlap integral therefore vanishes, the unshared pair is practically immobilised, and the nitrogen atom has almost no effect on the optical properties. Nevertheless, benzoquinuclidine is very different in basicity from quinuclidine, and is intermediate in basic strength between the latter and dimethylaniline[258].

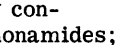


(I) (II) (III) (IV) (V)

Some data on the effect of angular rotation on conjugation effects are available for the system . Thus, *N*-methylpyrrolidone (III) has an almost planar b Od system, and shows distinct conjugation effects: the C=O frequency is lower than in cyclopentanone by 55 cm^{-1}, and $I_{C=O}$ is slightly higher[126]. On the other hand, in quinuclidone (IV), where the overlap integral of the *n* and π* orbitals is zero, $\omega_{C=O}$ is actually much greater than in bicyclo-(2,2,2)-octan-2-one (V).[259] We note that an increase in $\omega_{C=O}$ is usually observed on introducing electronegative substituents (for example, in RCOCl). These results suggest that a given group can behave either electropositively or electronegatively depending on its angle of rotation. It is interesting to note that the basicity of quinuclidone (IV) is much lower than that of quinuclidine[259] in spite of the unfavourable geometry of the N–C=O system from the point of view of conjugation.

Not surprisingly, all evidence of $n-\pi$ conjugation in aromatic amines disappears on forming salts: see the data for $PhNR_2$ and $PhNR_2H^+$ in Table 4.

In Π–OR and Π–SR systems, n,π conjugation is most evident when the fragments are in the same plane. Conjugation is very weak in non-planar mesityl compounds. It has been pointed out[260] that the sulphur atom has both donor properties (resulting from the unshared electron pair) and acceptor properties (resulting from the vacant 3*d* orbital). In some systems the donor properties are almost absent, but the acceptor properties persist because $\pi-d$ overlapping is retained.

Some data suggest a difference in conjugation behaviour between *s-cis* and *s-trans* isomers. Simple vinyl ethers have mainly the *s-trans* form, and they show low $\omega_{C=C}$ and $K_{C=C}$ values and high $I_{C=C}$ values as a result of the influenee of OAlk;[15,226,255] no such behaviour is found with compounds of the type .[261] In the analogous cyclic compound of sulphur both $\omega_{C=C}$ and $I_{C=C}$ are modified[261], but in every case they are lower than in the open-chain molecule[225].

XI. $\pi-\pi$ CONJUGATION

Molecules with alternating multiple and single bonds usually show a small decrease (0–20%) in the rigidity of the multiple bonds and a more substantial increase (up to 30%) in the rigidity of the intervening single bonds, which has been ascribed partly to atomic orbital hybridisation phenomena and partly to some measure of double bond character (nitrobenzene[262], diacetylene[263,264], glyoxal, acrolein[114], butadiene[113,265], and to a lesser extent diacyanogen[113]). However, different authors have obtained entirely different quantitative results. Some workers conclude that the off-diagonal force coefficient which characterises the interaction of the two π-bonds has a large, negative value[113,114,263]; this implies that the stretching of one π-bond induces an additional force field in the other π-bond, tending to elongate it[101].

The clearest evidence of $\pi-\pi$ conjugation comes from the increased intensity of Raman lines—in particular, the lines associated with stretching vibrations of conjugated multiple bonds. There are some early qualitative reports[266] of unusually strong lines from C=C and C=O double bonds in the presence of conjugation. Quantitative measurements of $I_{C=O}$ in acetophenone and benzophenone[215], I_{NO_2} in nitrobenzene, nitronaphthalene, and nitroaniline, $I_{C\equiv N}$ in benzonitrile and vinyl cyanide, and $I_{C=C}$ in styrene, vinyl cyanide, acrylates, butadiene, and hexatriene[15,28] have shown that a high intensity is characteristic of coplanar systems of alternating multiple and single bonds[28]. An unusually strong C≡C line has been

observed in phenylacetylene [37,229]. When an electronegative group (CN, NO_2, COR) is combined with a system of CC π-bonds, the lines of both fragments show an abnormally high intensity (particularly those of the electronegative group).[28] Oxalates [200,220], and vinyl and phenyl sulphones [219,227,231], show no enhancement of refraction or of Raman line intensity in spite of the non-additivity of the dipole moments in phenyl sulphones (see Tables 3 and 4).

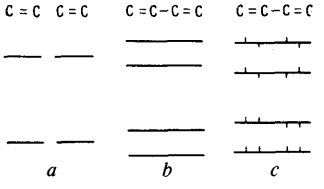


Figure 7. Filled and vacant π orbitals in the C=C-C=C system: *a*) in the absence of conjugation, *b*) and *c*) in the presence of conjugation for two extreme positions of the C atom ("symmetric C=C vibration"). The vertical strokes in diagram *c* denote the sign of the AO contributions.

Experiment has shown that $I_{C=C}$ is approximately 10 times higher in butadiene than in mono-olefins, and 10 times higher still in the triene [15]. Further increase in the number of conjugated double bonds makes the intensity progressively higher [12].

Studies of the absorption spectra and of $I(\nu)$ lead to the conclusion that the difference in ν_e between butadiene and mono-olefins is sufficient to account for a four-fold increase in intensity. If account is taken also of differences in oscillator strength, in the amplitude of the natural coordinates, and in the anisotropy, the ten-fold increase in intensity in butadiene can be explained by applying formula (2).[35] It should be noted that after the transition of an electron to the lowest vacant orbital (π_3^*), the equilibrium value of q_{C-C} should decrease a little and that of $q_{C=C}$ should increase (though by less than in the corresponding $\pi \rightarrow \pi^*$ transition in mono-olefins). The same conclusion follows from the fact that the wave function of π_3^* has nodal points in the region of the double bonds but not in that of the intervening single bond (see Fig. 7). Thus, the equilibrium value of the normal nuclear coordinate for the "stretching symmetric vibration of the C=C bonds" should by changed by electronic excitation, and $\partial\nu_e/\partial Q$ should be non-zero. Systems with different numbers of conjugated double bonds are discussed in detail in Ref. 12.

Facer and Thompson [129] have proposed a formula for the intensity, including terms which allow specifically for the effect of "mesomerism" and for the shift in ν_e, and appear to be unsoundly based.

Calculations for the butadiene molecule by various MMO variants give a π order of between 0.15 and 0.5 for the central C–C bond and between 0.8 and 0.95 for the double bonds. It is stated [267,268] that the alternation of bond orders and force constants [113,269] found in butadiene is retained almost unchanged in the polyene chain. The decrease in the "C=C vibration" frequency with increase of chain length is due to a slightly increased contribution from ordinary bond vibrations, not to a change in $K_{C=C}$.

An increase in the length of the polyene chain has little effect on $\omega_{C=O}$, but it leads to a rapid increase of $I_{C=C}$ and $I_{C=O}$, with extremely high values under resonance conditions, when the frequency of the exciting light (22 938 cm^{-1}) is in the region of the absorption band. With still further increase in chain length the band in the electronic absorption spectra is shifted towards the red and the intensity of the Raman lines (as expected from theory) begins to fall off. The very high intensity obtained by resonance excitation of the spectra of polyenes is due to the relatively small damping constants ($\gamma < \omega$!).

Table 6.

n	$\omega_{C=C}$	$I^s_{C=C}$	$\omega_{C=O}$	$I^s_{C=O}$	ν_e
0	—	——	1760	40	——
1	1664	300	1733	350	48 100
2	1643	5000	1726	800	38 500
3	1620	30000	1721	1800	33 700
4	1597	150000	1717	6000	30 400
5	1572	$1.2 \cdot 10^6$	——	——	28 200
6	1562	$17 \cdot 10^6$	——	——	26 300
7	1550	$400 \cdot 10^6$	——	——	24 800
8	1540	$200 \cdot 10^6$	——	——	23 300
10	(1500)	$(50 \cdot 10^6)$	——	——	(20 500)

Data [12,76] for the C=C and C=O lines of the series of compounds EtOOC–$(CH{=}CH)_n$–COOEt (in acetone) are set out in Table 6 together with the position of the main u. v. absorption band (ν_e, cm^{-1}). Values shown in brackets are tentative extrapolations. The u. v. spectra are shown in Fig. 8.

Vol'kenshtein and Yazykova [270] have tried to calculate $I_{C=C}$ for a molecule with conjugated C=C bonds by using the metal model (π-electron approximation); the symmetric vibration of the double bonds was modelled by simply changing the length of the potential well, leading to a change in ν_e. Savin [271,272] applied the π-electron approximation to a single electronic transition, and described the changes in ν_e induced by the vibration of the atoms in the chain by taking account of the coefficients for the type of vibration. In the final variant, the potential was assumed uniform along the chain. Good qualitative agreement with experiment was obtained in both these investigations.

It should be possible to calculate α and α' under non-resonance conditions for any (not too complex) molecule, irrespectively of whether the additive scheme or the free-electron model is applicable, by computing the electronic energy levels and transition probabilities for all the electrons, and their interactions. Of course, calculations based on MMO LCAO are not very precise, but they have some predictive value.

Contradictory views have been expressed on the role of the inductive effect in molecules with conjugated multiple bonds. The question can be answered with greater confidence by comparing molecules in which the mutual orientation of the fragments is different, for example in the "benzene ring–nitro group" system. The deviations from additivity in the optical properties, dipole moments, and many other parameters of the planar, unsubstituted nitrobenzene molecule (the angle of rotation of the nitro group about the C–N bond is $\theta = 0°$) are quite substantial.

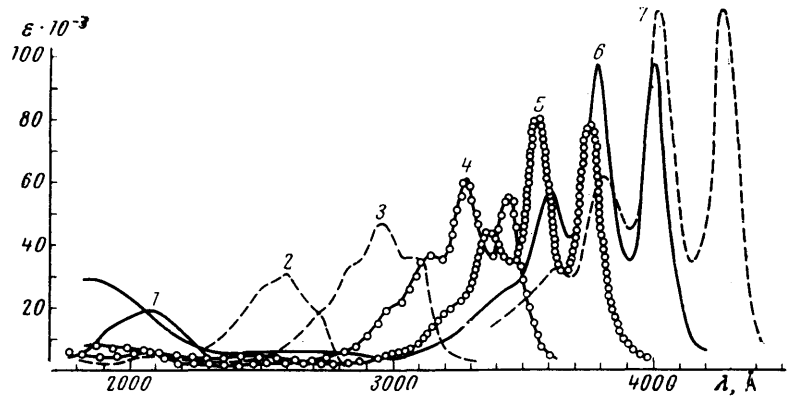


Figure 8. Absorption spectra of heptane solutions of EtOOC-(CH=CH)$_n$-COOEt. The value of n is shown on the curves.

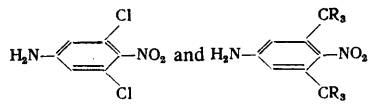
The introduction of substituents in the *ortho*-position increases the value of θ to a greater or lesser extent, which can be calculated from the force field. We express[95] the potential energy of the molecule as

$$U = U_0 + U_u + U_{def} + U_\theta,$$

where U_0 is the energy of the planar molecule in the presence of conjugation and in the absence of steric hindrance, U_u is the energy expended against forces acting between unbound atoms, U_{def} is the energy needed to deform the bond angles, and U_θ is the conjugation energy. U_{def} can be determined by introducing angular force constants, U_u can be determined by means of the Lennard-Jones potential function. A knowledge of the van der Waals radii is not sufficient, because the atoms are not rigid spheres; furthermore, the potential is influenced by any excess of positive or negative charge on the atoms. This explains, at least in part, why Cl, Cl *ortho*-substituents affect the rotation of the nitro group more strongly than CH_3, CH_3, whereas the converse is true of the rotation of the NR_2 group[95].

Table 7 shows a set of data[95,273] for derivatives of nitrobenzene: a) the difference between the nitro-group frequency of the given compound and that of unsubstituted nitrobenzene (1348 cm^{-1}, in benzene solution); b) the intensity I^S of the line of the nitro group (in benzene solution); c) the absorption coefficient at 2500 Å (in heptane solution); d) the deviation from additivity in the dipole moment; e) the estimated angular rotation θ of the nitro group. The figure in brackets is a tentative estimate.

It is evident from Table 7 that the mutual effect of Ph and NO_2 is almost completely suppressed when the angle θ is large. The interaction between the nitro group and substituents in the *para*-position also has been shown to be weakened, for example in the molecules[257,274]



In the latter compound the calculated rotation[274] is $\theta = 80°$, and the intensity of the first strong u. v. band is decreased by a factor of 20. It is interesting to note that the rotated nitro group retains some of its effect on the basicity of the amino group: this is ascribed[274] to the fact that the inductive effect persists even though conjugation has disappeared.

Thus, we may conclude that, in spite of the large polarity of the nitro group, the inductive effect has a negligible influence on the rigidity of chemical bonds in aromatic nitro compounds, on their dipole moments, or on their optical properties, but a large effect persists on the rate constants of chemical reactions with an ionic mechanism.

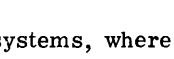
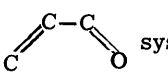
Table 7. Spectra of X-C$_6$H$_4$-NO$_2$ compounds in nitropropane.

Group X	$\Delta\omega$, cm^{-1}	I^S	ϵ_{2500}	$\Delta\mu$	θ
H	0	700	9600	0.8	0
CH_3	17	250	1900	0.4	55°
Cl	14	50	1300	0.1	70°
Br	10	50	3500	0.1	—
$C(CH_3)_3$	29	(40)	800	—	75°
$PrNO_2$	36	35	—	0	—

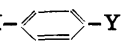
On going from trichloronitrobenzene to tribromonitrobenzene, I_{NO_2} decreases (as expected), but ϵ_{2500} increases. It is evident that the "benzene ring–bromine atom" system is beginning to dominate the u. v. spectra, so that any information regarding conjugation with the nitro group is lost. It is equally difficult to detect disturbance of the conjugation from $\Delta\omega$ values, because the frequency is affected by the mass of the halogen atoms. The I^S values are not significantly affected[95] by these factors. Egorov and coworkers[196] have published some interesting results on non-planar fluoro-derivatives of stilbene.

Planar *s-trans* and *s-cis* systems show some interesting differences in the conjugation of their double bonds. The intensity of the C=C lines in diene systems of the *s-trans* type is approximately twice as high as that of the *s-cis* systems[275,276]. This is partly due to the lower contribution of anisotropy in α' to the observed intensity

in the *s-cis* systems. The force field is very different in the two cases, as shown by the relative frequencies of the two forms of stretching vibrations of the double bonds: in *s-cis* dienes (as opposed to *s-trans* dienes) the antisymmetric vibration has the higher frequency, possibly as a result of differences in the off-diagonal force coefficients. The effect of conformation on $I_{C=C}$ is particularly strong in trienes [275].

In  systems, where the C=C and C=O vibrations are fairly well separated [114,277], $I_{C=O}$ is large [15,98,278], and in  systems $I_{C=C}$ is large [277]. In the latter case the vibrations are less localised: the higher frequency, and more substantial contribution from the C=O bond, are assigned [279] to the "anti-phase" vibration of the double bonds, and hence the intensity of the line is small.

Many papers have been published on cyclic diene systems [44,234,275,276,280,281] and on open-chain diene compounds [205,281,282].

XII. CONJUGATION IN X--Y MOLECULES

In compounds of the X-C_6H_4-Y type, changes in the frequency ($\Delta\omega_Y$) of the quasi-local vibration of the group Y under the influence of X can be used directly as an approximate criterion of changes in the rigidity of the chemical bond, which can be as high as 10%. Difference of 2–4 cm^{-1} in ω_Y are significant in this respect. The effect on the frequency and on the stiffness of the bonds is most marked for a pair of substituents one of which is an electron donor of the first type in Section V, the other an acceptor (a *k*-acceptor and a *k*-donor in the writer's terminology [109,110]); the effect is smallest when the two substituents are of the same type. The same is true of the deviations in additivity of the dipole moments and of the specific features of Hammett's σ constants. These effects are illustrated in Fig. 9, which shows the correlations between $\Delta\omega_Y$ and the donor–acceptor properties of the group X, characterised by the deviations from additivity in the dipole moments of the molecules PhX. (A positive value of $\Delta\mu$ corresponds to a shift of the electron density from X towards Ph.) The data for NO_2 and NH_2 are arithmetic means of $\Delta\omega^S$ and $\Delta\omega^{as}$. These curves were drawn from measurements of ω in CCl_4. [225,231,283,284] The influence of X on ω_Y is sometimes enhanced by solvation in more "active" solvents, and is less marked when the molecules are isolated as in vapours (see the data for *p*-nitroaniline and other similar compounds [124]).

As regards the influence of substituents on the intensity, the conjugation conditions (in particular, the number of conjugated bonds) are the determining factor for the Raman lines of multiple bonds. Thus, the vinyl group (or a whole system of CC π-bonds) in position X has a negligible effect on the frequency of the lines for the double bonds of the group Y (a few cm^{-1}), but it has a powerful effect on their intensity, which may change by a factor of 1000. This phenomenon is closely bound up with the effect on ν_e.

The large decrease in the frequency ν_e of the first u. v. absorption band when X and Y groups of different types are combined can be explained by considering the energetics of the orbitals of the fragments and of the MO of the X–Π–Y system (see Fig. 6 of Ref. 224). A decrease in ν_e has a direct effect on I_Y, but changes in ν_e' and f_e' are also important (see Section II). Some calculations can be found in Ref. 235.

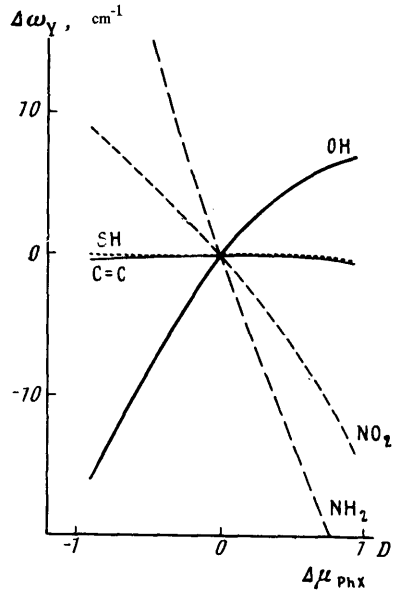
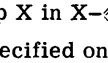
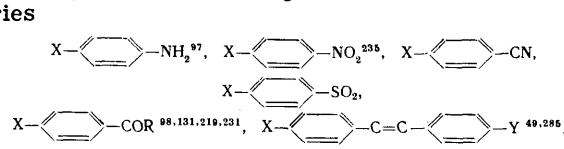


Figure 9. Change in ω_Y under the influence of the group X in X--Y compounds; the group Y is specified on the curves.

A comparison of various parameters of molecules in the series



has revealed a number of correlations between deviations from additivity in the dipole moments, the $\Delta\omega_Y$ values, and the Hammett constants (σ) for the group X. [97] On the other hand, approximate correlations have been observed between the various manifestations of the mutual effect of the groups X and Y in different optical properties [235]: the greater the deviations from additivity in the effects of X and Y on the u. v. spectra, the more prevalent are large values of I_Y (at least for the lines from double and triple bonds), exaltation of molecular refraction, and dispersion of the refractive index. However, various attempts to establish simple relationships between pairs of the above parameters (e.g. between I_Y and σ_X) have been successful only over a very limited range of compounds (see Ref. 66 and 138).

XIII. CONJUGATION WITH A THREE-MEMBERED RING

Compounds containing a three-membered ring show certain similarities with olefins in chemical properties (for example, in addition reactions involving ring-opening).

Their physical and chemical properties suggest interaction between the three-membered ring and systems of double bonds. A significant increase in the intensity of the Raman lines due to multiple bonds and to the three-membered ring has been observed in cyclopropylketones [201], vinylcyclopropane [286,287], phenylcyclopropane [218,243], and glycidates [127]. It is interesting to note that in *p*-dicyclopropylbenzene the intensity of the line for the benzene ring (I_{1600}) is even higher than in phenylcyclopropane: the behaviour is similar to that of a conjugated chain [243].

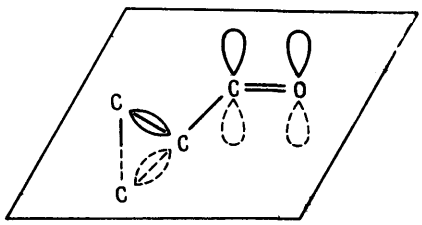
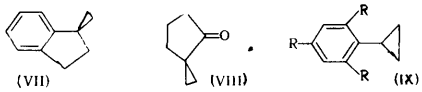


Figure 10. Disposition of the orbitals in the spirocyclopropancyclopentanone ("three-membered ring–double bond") system.

Phenylcyclopropane and *C*-phenylethyleneimine are intermediate between toluene and styrene (see Table 4) in their I_{1600} value and in their u. v. spectra. This evidence of conjugation has been ascribed [288] to hybridisation of the AO of the carbon atom in the three-membered ring, leading to some measure of sp^2 character. The valency electrons which form the ring are assumed to have some π-electron character. The configuration in which the three-membered ring and the π-bond system are in mutually perpendicular planes (see Fig. 10) is most conducive to conjugation [286]: this is found, for example, in spirocyclopropanindane (VII) [288] and spiro-cyclopropancyclopentanone (VIII). [289] In mesitylcyclopropane (IX) the optimum conformation from the point of view of conjugation cannot be achieved, and in this compound I_{1600} is hardly greater than in mesitylene, which suggests that conjugation is almost entirely absent [287].



(VII) (VIII) (IX)

If the C<(C,C) plane in isopropylbenzene is perpendicular to the plane of the benzene ring, the highest filled σ-orbital of C<(C,C) can overlap the *p*-orbital of the C_{ar} atom. However, significant perturbation and combination of the wave functions is precluded by the large difference in energy of the orbitals of the two fragments. These effects can occur, however, with the cyclopropyl group, because of the lower energy of its $\sigma \rightarrow \sigma^*$ transition.

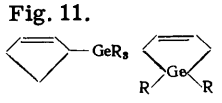
According to Bent [290], the electronegative nitrogen atom in *C*-phenylethyleneimine should enhance the *p*-character of the bonds in the three-membered ring. This is not confirmed by an analysis [218] of Raman line intensity data.

In *N*-phenylethyleneimine, Ph–N<(C,C), I_{1600} is determined mainly by n,π conjugation, which is controlled by the rotation of the three-membered ring. This compound differs from phenylcyclopropane in having the two C atoms on the same side of the Ph plane. I_{1600} for *N*-phenylethyleneimine is lower than the value for $PhNR_2$ by almost a factor of two: this is ascribed [218] to the more pronounced *s* character of the unshared electron pair of the nitrogen atom.

XIV. SYSTEMS WITH A BRIDGING ATOM (П–M–Z). σ–π CONJUGATION

Systems of bonds with a bridging atom are extremely interesting. They include some radicals found in the majority of organic compounds. In a number of systems of the type П–CH_2–Z and similar systems with different bridging groups (П–M–Z), the influence of Z is as strong as in the system П–Z (see Tables 4 and 5). [232,244] However, the special features of the effect are different in the two cases. Thus, the N atom of the amino group has a strong effect on the spectra in П–Z systems, but practically none in П–CH_2–Z systems, whereas the opposite is true of the Hg atom. The presence of an unshared electron pair in Z, and the polarity of the substituent, have only a minor significance in systems with a methylene bridge, but heavy atoms have an important effect [220,232,291]: within a given period of the Periodic Table, the effect of Z on the Raman and u. v. spectra of Ph–C–ZR_n, C=C–C–ZR_n, and other similar systems increases somewhat on going from right to left [291]. This tendency is most marked with compounds which include a *k*-acceptor group—for example, ROC–CH_2–ZR_n—since conditions are then favourable for donor–acceptor interactions and the rigidity of the double bond is decreased more substantially [245] (see Table 5, which lists $\omega C{=}C$ and I_{1600} for the corresponding allyl and benzyl compounds).

It has been shown [291] that as the atomic weight of the atom Z increases (within a given sub-group of the Periodic Table) the effect of the substituent on the optical properties of П–CH_2–Z systems increases and the frequencies ν_e of the u.v. π–π^* bands decrease. Under these conditions molecules which are known to be non-planar (as opposed to π,π conjugated systems) show the largest deviations from additivity. Thus, compound (X) has Raman and u.v. spectra [245,291,292] ($I^S_{C=C} = 160$ [292]) very different from those of cyclopentene ($I^S_{C=C} = 28$), whereas molecule (XI) which has an almost planar ring is similar to cyclopentene ($I^S_{C=C} = 25$ for (XI) [292]). The u.v. spectra of these compounds are shown in Fig. 11.



(X) (XI)

These spectra repudiate [292] the view [293,294] that the key role is played by the overlap of two *p*-orbitals of the C atoms adjacent to the double bond with a *d*-orbital of the Si atom (C=Si) or with Hg orbitals in systems like C=C–C–Z.

None of the above experimental results, including those concerning angular dependences, in any way conflicts with the view that σ–π conjugation can be ascribed

to the overlap of the wave functions of the double-bond π-orbitals with the two-centre orbital of the C–Z σ-bond (or the multi-centre orbital of the C–Z group). When the σ-bond is in the plane of the π-bond system (in the nodal plane of the p-orbitals) the overlap vanishes, and when it is at right angles to this plane the overlap is a maximum. On the other hand, when the orbital energies of conjugated π and σ bonds are similar, and the latter bond includes a heavy atom Z, combination of the wave functions is favoured [291]. Several authors have studied the system R_3Si-CH_2-COR, and have variously concluded that the most important effect is the inductive effect [250], the interaction between the unshared electron pair of the oxygen atom and the vacant Si–orbital [295], or the presence of a resonance structure of the type $Si^+C=C-O^-$ (see Ref. 250). In benzyltin and other similar compounds the inductive effect [296] or p_π-d_π conjugation [293,327] are the most important.

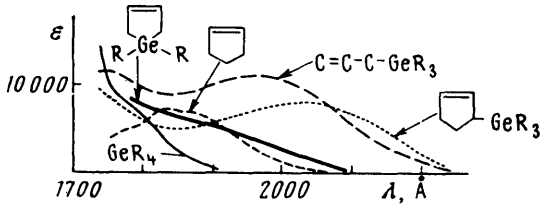
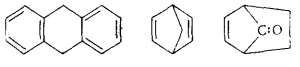


Figure 11. U. v. absorption spectra (in heptane solution).

The virtual absence of σ-π conjugation effects in ordinary open-chain organic molecules containing C, H, N, O, and Cl atoms is due to the high energy of the $\sigma \rightarrow \sigma^*$ transition and therefore to the small contribution of the C–Z σ-bond to the highest filled and the lowest vacant MO; the low conjugation energy ($< kT$) does not allow the bonds to take up the orientation most favourable to conjugation.

In systems of the type $\Pi-CH_2-\Pi'$ the deviations from additivity in the Raman (and also the u.v.) spectra are quite insignificant. (The systems which have been investigated include Ph–C–Ph, Ph–C–C–Ph, [220] Ph–C–C=C, [161] C=C–C–C=C, [281] Ph–C–CN, [232] and limonene [15].) However, when the fragments have some well defined orientations (as in tripticene, where the planes of the three benzene rings are at 120° to each other) the first u.v. absorption band has a high intensity [297]. In dihydroanthracene (XII), norbornadiene (XIII), and other similar compounds the anomalies are not very marked; it has been suggested [298] that in these molecules the two electronic oscillators are weakly coupled.



(XII) (XIII) (XIV)

Most workers consider that the most important effect in this type of molecule is the overlap of the p orbitals of the two nearest carbon atoms from different fragments. Depending on the orientation of these AO, large differences in the perturbation of the electronic levels are possible. Thus, in system (XIV) the p orbital of the C atom of the carbonyl group partly overlaps the C=C π orbital (but not the π^*, which has a nodal point in the middle of the double bond). On the other hand, the AO of the unshared electron pair of the oxygen atom overlaps the π^* orbital (though to a very small extent). Hence, the energies of the various electronic transitions are affected in different ways. In the spirene molecules the systems of double bonds lie in mutually perpendicular planes, but some interaction can nevertheless take place; in spiro-nonatetraene we expect interaction between the highest filled and also the highest vacant orbitals of the fragments [299] (see Fig. 12).

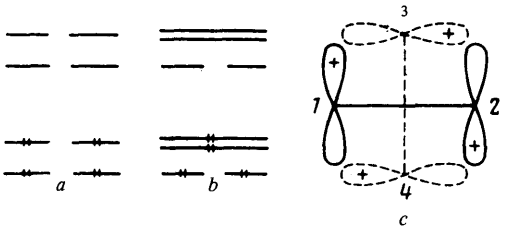
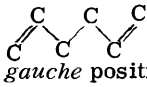


Figure 12. Energy of the π orbitals in the  system: *a*) for the two separate fragments; *b*) in the presence of interaction between the fragments; *c*) p orbitals of the carbon atoms *1*, *2*, *3*, *4* (the observer is looking along the symmetry axis *4*). The signs correspond to the upper filled MO.

Cookson [300] considers a system of bonds of the type . If the central C–C bond is in the *gauche* position with respect to each of the double bonds, its σ orbital is assumed to overlap the π orbitals of the two C=C bonds, with the possibility of splitting of the π electron levels and "σ-coupled π-electron transitions". Under these conditions the C–C σ bond takes practically no part in the electronic transition but it allows delocalisation of the transition.

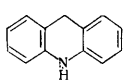
In molecules of the type $X-CH_2-Y$ where X is an electron-donor group of the first type (see Section V) and Y is an electron-acceptor group of the second type, donor-acceptor interaction can occur with increase in the multiplicity of the X–C bond and a corresponding decrease in the multiplicity of the C–Y bond. Under favourable conditions, ions can be formed: $(X^+=CH_2) + Y^-$ (for example, $R_2N^+-CH_2-Cl \rightarrow (R_2N^+=CH_2) + Cl^-$, see Ref. 301). The combination of a donor group of the second type and an acceptor group of the first type gives, in the extreme case, the structure $X^+ + (CH_2=Y^-)$, as in $K^+ + (CH_2=NO_2^-)$.

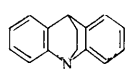
The cyano group has weaker acceptor properties of the second type than has the Cl group; accordingly, the molecule $R_2N.CH_2.CN$ does not form ions similar to those suggested above for the chloro compound. However, their Raman spectra show a fairly large drop in ω_{CN} and in the rigidity of the C≡N bond; the characteristic absorption band of the amino group at 1900–2000 Å ($n \rightarrow \sigma^*$ transition) is considerably weakened, and the basicity of the amino group is decreased. All these effects are consistent with the participation of the unshared electron pair of the amino group in conjugation of the type described above [232]. Similarly, it has been shown [302] that the N–C bond is shortened and the C–CN bond in lengthened even when the orbitals of the triple bond and of the unshared

pair on the amino nitrogen cannot overlap. The influence of the amino group on ω_{CN} is much smaller in compounds of the type p-R_2N-C_6H_4-CH_2-CN than in R_2N-CH_2-CN, but it can be detected [303]. The effect is entirely absent in the analogous carbonyl compounds, showing that COR has a very low capacity as an electron acceptor [232].

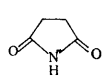
Data on compounds with -O-, -S-, and -NH- bridges and fragmentary and sometimes contradictory. Most of the work has been done on compounds of the Ph-M-Ph type, particularly diphenylamine, which in spite of lack of coplanarity, and some "competition" between the two electron acceptors, shows clear evidence of non-additivity: I_{1600} is higher than in aniline by a factor of 6 (see Ref. 220, where the u.v. spectra are also given). According to the u.v. spectra, the same deviations from additivity are found in acridan (XV). The Raman spectra indicate considerable interaction between the double bonds in N-vinylpyrrolidone. Acetanilide has very strong lines from the C=O group and the benzene ring; in the spectrum of Ph.NR.COR the symptoms of n-π conjugation with the carbonyl group are enhanced, and those of conjugation with the benzene ring are suppressed. This observation has prompted the conclusion that the angular rotation of the NRCOR group relative to the Ph plane is increased, and that conjugation in the N-C=O system is strengthened [126].

The main contribution to interaction in nitrogen-bridge systems comes from the unshared electron pair of the nitrogen atom, which is determined by the relative orientation of the fragments (see above). In the dibenzoquinuclidine molecule (XVI) the unshared pair is immobile, and as a result of this the spectroscopic evidence of interaction between the benzene rings and of n-π conjugation is almost totally absent [304].


(XV)


(XVI)


(XVII)


(XVIII)

Π-S-Π′ systems have smaller deviations from additivity than the corresponding nitrogen-bridge systems. Nevertheless, $I_{C=C}$ for C=C-S-C=C was found to be at least double the value expected on the assumption of full additivity [223,280]. Judging from the u.v. spectra [305], the effect should be even greater in thiopyran (XVII). However, the carbonyl group in the C=C-S-COR system is found [306] to have a negligible effect on $I_{C=C}$. No deviations from additivity can be detected in Π-SO_2-Π′ systems [223,280].

Even smaller anomalies were found in compounds with an oxygen bridge [15,223,226,239,307,308]. $I_{C=C}$, $I_{C=O}$, and I_{1600} are slightly enhanced in compounds with the bond systems C=C-O-COR, Ph-O-C=C, and C=C-O-C=C, and an even more significant effect is found in $C_6H_5.C_6H_4.O.C{=}C$. In the presence of steric hindrance (for example, in mesityl vinyl ether) interaction effects are almost zero [223,239].

One interesting feature of the spectra of Π-M-Π′ systems with -O-, -S-, and -N- bridges is the fact that the frequencies of the π bonds adjacent to the bridging atom are higher (by 5-10 cm^{-1}) than the corresponding frequencies for Π-M-R and R-M-Π′ compounds; this effect may be due to the increased rigidity of the bonds, and possibly also to the contribution of off-diagonal elements [112,115]. In succinimide (XVIII) and in succinic anhydride the off-diagonal element corresponding to the interaction of the two C=O groups is fairly large; this element is related to the interaction conditions in the two n-π conjugated systems [112].

Very little is known about the influence of heavy atoms in Π-O-Z, Π-S-Z, and Π-NH-Z systems. In systems of this type, n-π conjugation favour a planar conformation, which in turn excludes σ-π conjugation. Mesityl compounds are known to be non-planar, with large θ angles, but no other information is available. Heavy atoms have been shown [291] to have less effect on the u.v. spectrum of the benzene ring in Ph-O-Z systems than in Ph-CH_2-Z systems. The u.v. spectra of Ph-NH-SiR_3 do not differ significantly from those of Ph-NH-R. [309] Various workers [187,188,283] have found that the mercury atom in the -Hg-CN system has little influence on $\partial\alpha/\partial q$ for the C≡N bond, but its effect is quite large in -Hg-S-CN systems.

No departures from additivity have been observed in $Si(HC{=}CH_2)_4$, $Si(C{\equiv}CH)_4$, and other similar Si compounds, but the influence of heavy atoms through the Si bridge is apparently even greater than through the methylene bridge. Whereas the u.v. spectra of PhR and $PhSiR_3$ are practically identical, the compound $Ph.SiR_2.SiR_3$ (where the Si-Si bond is believed to form a large angle with the plane of the benzene ring) shows a large bathochromic shift of the u.v. band [93], which increases with the length of the chain of silicon atoms [310]. Since such chains give rise to a distinct closing-up of the electronic levels, conditions become favourable for combination of the wave functions of Ph and the substituent [93] (Sakurai and Kumada [311] have termed this a dative p_π-d_π bond). Non-additivity is particularly evident in the spectra of Ph-$(SiR_2)_n$-Ph when n is large [312]; it is independent of the parity of n and indicative of direct participation of the orbitals of the bridging atoms in the conjugation. The interaction of benzene rings through the Sn-Sn group has been ascribed [313] to participation of the d orbitals of Sn, and in a similar way [242] the interaction through a boron atom has been ascribed to the participation of the $2p$ boron orbital.

The mutual influence of atomic groups in molecules of the type Π-M-Π′ and Π-M-Z is far from being fully understood, and widely different hypotheses and conclusions are currently being discussed. From the whole of the available data it would appear that interaction can take place by a number of different paths, including: 1) direct overlap of the orbitals of relatively close atoms of the groups Π and Π′ or of the orbitals of Π and Z; 2) participation of the orbitals of bridging atoms in the delocalised orbitals of the molecule (for example, in systems with σ-π or π-σ-π conjugation); 3) non-additive interactions (e.g. in n-π conjugation) in Π-M and M-Π′ systems, particularly as regards the population of the AO of the bridge.

Spectroscopic data on conjugation in systems of ordinary bonds are very scarce. U. v. spectral data suggest that the intensity of Raman lines for the chains $(SiR_2)_n$, $(GeR_2)_n$, and $(SnR_2)_n$ should be strongly non-additive [93]. The intensity of the C-I line has been found [314] to be much greater in the I-CH_2-CH_2-I spectrum than in the I-$(CH_2)_3$-I spectrum.

XV. APPLICATIONS OF RAMAN LINE INTENSITY STUDIES

The previous Sections have been concerned with the application of Raman line intensity data to the study of mutual effects of atomic groups. In addition, a great deal of work has been done on the application of line intensity data to the choice of the correct structural formula for new compounds (see examples in Ref. 315), to determine

conformation, to study tautomerism, association, ionisation, and symmetry in molecules, and also to assign spectral lines to particular types of vibration (see examples in Ref. 15).

Bobovich and coworkers have established the structure of various products which could not be characterised by chemical methods[316-318]. By measuring the intensity of the lines for the benzene ring, the double bonds, and the nitro group in the products of the reaction of bromonitrostyrene with β-dicarbonyl compounds, they were able to choose the correct structure from four possible alternatives, to disprove the originally suggested structure involving conjugation of the nitro group and the phenyl group, and to establish the presence (and the type) of enolisation[318]. The positions of the double bond in phenylaminotriazole and of the acyl group in its acylation products have been established[317]. Six C_6Cl_8 compounds have been assigned to well defined isomeric forms by choosing between fourteen possible structural formula (though not always convincingly)[319].

Shorygin and Alaune[237] have determined the position of equilibrium in salt formation in "aromatic amine + organic acid" systems. Thiocyanato complexes have been examined[188], with the conclusion that mercury is attached to the ligand groups through largely covalent bonds with S atoms, zinc is attached to the same atom through weakly covalent bonds (low value of α'), whereas cadmium is attached to C atoms. The spectra of nitrates in aqueous solution have been studied, and it has been shown that ion pairs ($Zn^{2+} + NO_3^-$) are formed in which the anion has a lower symmetry, and that a covalent bond exists in indium nitrate[320]. From the intensity of cyanate lines it has been suggested[253] that the Au–C bond has some double bond character. Association has been investigated in acetamide[221], benzene[130], and other compounds. The angular rotation of the fragments of the biphenyl molecule has been evaluated from the intensity of the benzene lines[321]. Other applications of Raman line intensity data include the determination of the relative amounts of *s-cis* and *s-trans* isomers in liquid pentenone[322], the determination of the energy difference between the *s-cis* and the *s-trans* isomers of acrolein[323], and the interpretation of u.v. absorption bands[324].

These examples are sufficient to indicate the versatility of the method; its possibilities are far from exhausted, and there is every reason to hope that effort in this direction will be intensified.

REFERENCES

1. Ya. S. Bobovich, Uspekhi Fiz. Nauk, 97, 37 (1969).
2. P. Hendra and P. Stratton, Chem. Rev., 69, 325 (1969).
3. J. Loader, "Basic Laser Raman Spectroscopy", Heyden, London, 1970.
4. J. Behringer and J. Brandmüller, Z. angew. Phys., 14, 674 (1962).
5. Ya. S. Bobovich and Ya. A. Eidus, Optika i Spektrosk., 16, 424 (1964).
6. J. Brandmüller, H. Hacker, and H. W. Schrötter, Chem. Ber., 99, 765 (1966).
7. F. Gandini, H. Moser, and F. Perzl, Z. angew. Phys., 23, 461 (1967).
8. B. Schrader and M. Stockburger, Naturwiss., 52, 298 (1965).
9. R. F. Schaufele, J. Opt. Soc. Amer., 57, 105 (1967).
10. G. N. Zerbi and P. Hendra, J. Mol. Spectroscopy, 27, 17 (1968).
11. P. P. Shorygin and T. M. Ivanova, Optika i Spektrosk., 15, 176 (1963).
12. P. P. Shorygin and T. M. Ivanova, Optika i Spektrosk., 25, 200 (1968).
13. S. K. Freeman and D. O. Landon, Analyt. Chem., 41, 398 (1969).
14. M. Delahaye, Applied Optics, 7, 2195 (1968).
15. P. P. Shorygin, Izv. Akad. Nauk SSSR, Ser. Fiz., 12, 576 (1948).
16. P. P. Shorygin, Uspekhi Khim., 19, 419 (1950).
17. P. P. Shorygin, Zhur. Fiz. Khim., 15, 1072 (1941).
18. G. P. Buyan, I. I. Kondilenko, and V. E. Pogorelov, Optika i Spektrosk., 27, 248 (1969).
19. P. P. Shorygin, Zhur. Fiz. Khim., 23, 873 (1949).
20. P. P. Shorygin, Acta Physicochim. URSS, 16, 12 (1942).
21. P. P. Shorygin, Uspekhi Khim., 13, 90 (1944).
22. G. Placzek, "Rayleigh-Streuung und Raman-Effekt", in "Handbuch der Radiologie" (E. Marx, Editor), (Translated into Russian), Khar'kov, 1935.
23. P. P. Shorygin and L. L. Krushinskii, "Fizicheskie Problemy Spektroskopii" (Physical Problems in Spectroscopy), Izd. Akad. Nauk SSSR, Moscow, 1962, Vol. 1, p. 346.
24. G. S. Landsberg, P. A. Bazhulin, and M. M. Sushchinskii, "Osnovnye Parametry Spektrov KR Uglevodorodov" (Basic Parameters of the Raman Spectra of Hydrocarbons), Izd. Akad. Nauk SSSR, Moscow, 1956.
25. J. Brandmüller and H. Moser, "Einführung in die Raman Spektroskopie" (Translated into Russian), Izd. Mir, Moscow, 1964.
26. J. Behringer, "Theorie der Molekularen Lichtstreuung", München, 1967.
27. M. M. Sushchinskii, "Spektry KR Molekul i Kristallov" (Raman Spectra of Molecules and Crystals), Izd. Nauka, Moscow, 1969.
28. P. P. Shorygin, Zhur. Fiz. Khim., 21, 1125 (1947).
29. P. P. Shorygin and L. L. Krushinskii, Dokl. Akad. Nauk SSSR, 133, 337 (1960).
30. P. P. Shorygin, Pure Applied Chem., 4, 87 (1962).
31. D. G. Rea, J. Mol. Spectroscopy, 4, 499, 507 (1960).
32. P. P. Shorygin and L. L. Kruschinskii, Z. Physik, 150, 332 (1958).
33. P. P. Shorygin, Izv. Akad. Nauk SSSR, Ser. Fiz., 17, 581 (1953).
34. J. Behringer and J. Brandmüller, Ann. Physik, 4, 234 (1959).
35. P. P. Shorygin and L. Z. Osityanskaya, Dokl. Akad. Nauk SSSR, 98, 51 (1954).
36. H. Buyken, K. Klauss, and H. Moser, Ber. Bunsenges. phys. Chemie, 71, 578 (1967).
37. J. Behringer, Z. Elektrochem., 62, 544 (1958).
38. G. Schreiber, Spectrochim. Acta, 22, 107 (1966).
39. J. Brandmüller and E. W. Schmidt, et al., Spectrochim. Acta, 17, 523 (1961).
40. I. I. Kondilenko and V. E. Pogorelov, Optika i Spektrosk., 19, 41 (1965).
41. M. M. Sushchinskii and V. A. Zubov, Optika i Spektrosk., 13, 766 (1962).
42. M. Ya. Tsenter and Ya. S. Bobovich, Optika i Spektrosk., 16, 246, 417 (1964).
43. W. Hofmann and H. Moser, Ber. Bunsenges. Phys. Chemie, 68, 129 (1964).
44. E. G. Treshchova, D. Ekkhardt, and Yu. K. Yur'ev, Zhur. Fiz. Khim., 38, 295 (1964) [Russ. J. Phys. Chem., No. 2 (1964)].
45. P. P. Shorygin, Zhur. Fiz. Khim., 22, 1409 (1948).
46. P. P. Shorygin, Dokl. Akad. Nauk SSSR, 87, 201 (1952).

47. P. Choruiguine, J. Chim. Physique, 50, D 31 (1953).
48. P. P. Shorygin, Zhur. Fiz. Khim., 25, 341 (1951).
49. P. P. Shorygin and T. M. Ivanova, Dokl. Akad. Nauk SSSR, 121, 70 (1958).
50. L. N. Ovander, Optika i Spektrosk., 10, 420 (1961).
51. L. L. Krushinskii and P. P. Shorygin, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 497 (1963).
52. P. P. Shorygin and L. L. Krushinskii, Dokl. Akad. Nauk SSSR, 154, 571 (1964); Optika i Spektrosk., 17, 551 (1964).
53. V. A. Zubov, Z. M. Muldakhmetov, and M. M. Sushchinskii, Optika i Spektrosk., No. II, 324 (1963).
54. H. H. Hacker, Thesis, Münich, 1968.
55. A. Albrecht, J. Chem. Phys., 34, 1476 (1961).
56. M. C. Hutley and D. J. Jacobs, Chem. Phys. Letters, 3, 711 (1969).
57. L. L. Krushinskii and P. P. Shorygin, Optika i Spektrosk., 19, 562 (1965).
58. P. P. Shorygin and L. L. Krushinskii, Ber. Bunsenges. Phys. Chemie, 72, 495 (1968).
59. L. L. Krushinskii, Thesis, Minsk, 1962; Optika i Spektrosk., 14, 767 (1963).
60. I. I. Kondilenko, V. E. Pogorelov, et al., Optika i Spektrosk., 26, 203 (1969).
61. L. Bernard, J. Chim. phys. biol., 63, 722 (1966).
62. F. A. Savin, Optika i Spektrosk., 19, 555 (1965).
63. P. P. Shorygin and N. S. Andreev, Optika i Spektrosk., 23, 687 (1967).
64. N. S. Andreev and P. P. Shorygin, Optika i Spektrosk., 22, 714 (1967).
65. L. L. Krushinskii and P. P. Shorygin, Optika i Spektrosk., 11, 24, 151 (1961).
66. Ya. S. Bobovich and N. M. Belyaevskaya, Optika i Spektrosk., 22, 315 (1967); 19, 198 (1965).
67. H. W. Schrötter, Z. Elektrochem., 64, 853 (1960).
68. L. M. Kutsyna and P. P. Shorygin, Izv. Akad. Nauk SSSR, Ser. Fiz., 18, 682 (1954).
69. P. P. Shorygin, Proceedings of the International Conference on Spectroscopy, Bombay, 1967, p. 201.
70. V. A. Morozov and P. P. Shorygin, Optika i Spektrosk., 19, 289 (1965); 20, 214 (1966).
71. A. Kh. Khalilov and P. P. Shorygin, Zhur. Fiz. Khim., 27, 330 (1953).
72. Ya. S. Bobovich and V. V. Perekalin, Zhur. Strukturnoi Khim., 1, 313 (1960).
73. M. Harrand, Thesis, Paris, 1953.
74. W. Meier and F. Dörr, Applied Spectroscopy, 14, 1 (1960).
75. H. W. Schrötter and J. Brandmüller, "Advances in Molecular Spectroscopy", Pergamon, Oxford, 1962, p. 1128.
76. T. M. Ivanova, L. A. Yanovskaya, and P. P. Shorygin, Optika i Spektrosk., 18, 206 (1965).
77. J. Brandmüller and H. Hacker, Z. Physik., 184, 14 (1965).
78. H. Hacker, Spectrochim. Acta, 21, 1989 (1965).
79. W. Krasser and H. W. Nürnberg, Naturwiss., 54, 134 (1967).
80. R. J. Gillespie and M. J. Morton, J. Mol. Spectroscopy, 30, 178 (1969).
81. J. Behringer, Symposium "Molecular Spectroscopy", Plenum Press, New York, 1967.
82. B. Thery, M. Harrand, and P. Grammaticakis, J. Phys. Radium, 24, 297 (1963).
83. R. C. Leite and S. P. Porto, Phys. Rev. Letters, 17, 10 (1966).
84. J. F. Scott, R. C. Leite, and T. C. Damen, Phys. Rev., 188, 1285 (1969).
85. J. M. Worlock and S. P. Porto, Phys. Rev. Letters, 15, 697 (1965).
86. W. Holzer, W. F. Murphy, and H. J. Bernstein, J. Chem. Phys., 52, 399 (1970); Chem. Phys. Letters, 4, 641 (1970).
87. L. R. Nair and C. E. Hathaway, Phys. Letters, A30, 253 (1969).
88. P. P. Shorygin, Dokl. Akad. Nauk SSSR, 78, 469 (1951).
89. Ya. S. Bobovich and M. Ya. Tsenter, Optika i Spektrosk., 8, 45 (1960).
90. R. D. Fischer and E. R. Lippincott, Spectrochim. Acta, 6, 255 (1954).
91. M. J. Dewar, "Superconjugation" (Translated into Russian), Izd. Mir, Moscow, 1965.
92. N. D. Sokolov, Uspekhi Khim., 36, 2195 (1967) [Russ. Chem. Rev., No. 12 (1967)].
93. P. P. Shorygin, V. A. Petukhov, O. M. Nefedov, et al., Teor. Eksper. Khim., 2, 190 (1966).
94. L. A. Blyumenfel'd, V. I. Gol'danskii, et al., Zhur. Strukturnoi Khim., 8, 854 (1967).
95. P. P. Shorygin and Z. F. Il'icheva, Izv. Akad. Nauk SSSR, Ser. Fiz., 22, 1058 (1958).
96. P. P. Shorygin and Z. S. Egorova, Dokl. Akad. Nauk SSSR, 121, 869 (1958).
97. P. P. Shorygin, Problemy Fiz. Khim., 1, 164 (1958); Zhur. Fiz. Khim., 23, 1477 (1959) [Russ. J. Phys. Chem., No. 7 (1959)].
98. G. Michel and M. Renson, Spectrochim. Acta, 23A, 1435 (1967).
99. L. P. Krasonomolova and Yu. A. Kushnikova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 31 (1967).
100. L. V. Levchenko and Yu. A. Kushnikova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 52 (1964); No. 4, 13.
101. P. P. Shorygin and E. M. Popov, Zhur. Fiz. Khim., 38,1429 (1964) [Russ. J. Phys. Chem., No. 6 (1964)].
102. V. S. Kukina and L. M. Sverdlov, Optika i Spektrosk., 23, 550 (1967).
103. N. I. Prokof'eva, L. M. Sverdlov, and M. M. Sushchinskii, Optika i Spektrosk., 15, 464 (1963); 17, 374 (1964).
104. V. I. Vakhlyueva, S. M. Kats, and L. M. Sverdlov, Optika i Spektrosk., 24, 547, 643, 808 (1968).
105. L. M. Sverdlov, M. A. Kovner, and E. M. Krainov, "Kolebatel'nye Spektry Mnogoatomnykh Molekul" (Vibrational Spectra of Polyatomic Molecules), Izd. Nauka, Moscow, 1970.
106. A. I. Vogel and W. T. Cresswell et al., J. Chem. Soc., 514 (1952).
107. P. P. Shorygin and Z. S. Egorova, Zhur. Fiz. Khim., 32, 915 (1958).
108. A. V. Bobrov, Kh. E. Sterin, and E. V. Sobolev, Dokl. Akad. Nauk SSSR, 144, 81 (1962).
109. P. P. Shorygin, B. V. Lopatin et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2010 (1966).
110. P. P. Shorygin and B. V. Lopatin, Zhur. Fiz. Khim., 42, 450 (1968) [Russ. J. Phys. Chem., No. 2 (1968)].
111. P. P. Shorygin, Optika i Spektrosk., 21, 381 (1966).
112. P. P. Shorygin and E. M. Popov, Dokl. Akad. Nauk SSSR, 146, 1132 (1962).
113. E. M. Popov and G. A. Kogan, Optika i Spektrosk., 17, 670 (1964); Teor. Eksper. Khim., 1, 295 (1965).
114. V. I. Vakhlyueva and L. M. Sverdlov, Izv. Vys. Ucheb. Zaved. Fiz., No. 7, 146 (1968).
115. E. M. Popov, A. Kh. Khomenko, and P. P. Shorygin, Izv. Akad. Nauk SSSR, Ser. Khim., 51 (1965).
116. I. N. Yukhnovskii, Teor. Eksper. Khim., 3, 410 (1967).

117. S. Szöke, Acta Chim. Acad. Sci. Hung., 51, 183 (1967).
118. P. P. Shorygin and M. V. Vol'kenshtein, Izv. Akad. Nauk SSSR, Ser. Fiz., 5, 174 (1941).
119. H. J. Bernstein and G. Allen, J. Opt. Soc. Amer., 45, 237 (1955).
120. A. I. Finkel'shtein and P. P. Shorygin, Zhur. Fiz. Khim., 26, 1272 (1952).
121. E. R. Lippincott and I. P. Sibilia, J. Opt. Soc. Amer., 49, 83 (1959).
122. F. Vratny, Analyt. Chim. Acta, 23, 171 (1960).
123. L. V. Luk'yanova, Thesis, Moscow, 1955.
124. P. P. Shorygin and B. V. Lopatin, Zhur. Fiz. Khim., 39, 2868 (1965) [Russ. J. Phys. Chem., No. 12 (1965)].
125. P. P. Shorygin, Zhur. Fiz. Khim., 22, 897 (1948).
126. P. P. Shorygin, T. N. Shkurina, et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2208 (1959).
127. A. K. Shokanov and Z. M. Muldakhmetov, Symposium "Stroenie Molekul i Kvantovaya Khimiya" (Structure of Molecules and Quantum Chemistry), Kiev, 1970, p. 103.
128. T. P. Tulub et al., Optika i Spektrosk., No. II, 306 (1963); No. III, 324 (1967).
129. G. H. Facer and H. W. Thompson, Proc. Roy. Soc., A268, 79 (1962).
130. Yu. K. Borod'ko and Ya. K. Syrkin, Optika i Spektrosk., 9, 677 (1960).
131. G. Michel and R. Gueibe, Bull. Soc. chim. belges, 70, 323 (1961).
132. M. Wahl, Thesis, Munich, 1969.
133. G. Fini, P. Mirone, and P. Patella, J. Mol. Spectroscopy, 28, 144 (1968).
134. A. D. Dembitskii, T. N. Sumarokova, and M. I. Usanovich, Optika i Spektrosk., 15, 48 (1963).
135. Z. Kecki and T. Gulic-Krzywicki, Roczniki Chem., 38, 277 (1964).
136. S. Kurowski, Roczniki Chem., 39, 1899 (1965).
137. Yu. A. Kushnikov and L. V. Levchenko, Izv. Akad. Nauk KazSSR, Ser. Khim., No. 1, 121 (1958); No. 1, 54 (1962).
138. J. P. Jesson and H. W. Thompson, Proc. Roy. Soc., A268, 68 (1962).
139. S. Minc and S. Kurowski, Z. Elektrochem., 61, 833 (1957).
140. A. I. Sokolovskaya, Trudy FIAN, 27, 63 (1964).
141. W. R. Hess, H. Hacker, H. Schrötter, and J. Brandmüller, Z. angew. Phys., 27, 233 (1969).
142. J. Masso, Y. Harker, and D. Edwards, J. Chem. Phys., 50, 5420 (1969).
143. E. J. Rosenbaum and C. Cerato, J. Opt. Soc. Amer., 42, 670 (1952).
144. W. F. Wurphy, W. Holzer, and H. Bernstein, Appl. Spectroscopy Rev., 23, 211 (1969).
145. D. M. Golden and B. Crawford, J. Chem. Phys., 36, 1654 (1962).
146. H. W. Schrötter and H. J. Bernstein, J. Mol. Spectroscopy, 12, 1 (1964); 22, 122 (1967)
147. W. Holzer, J. Mol. Spectroscopy, 25, 123 (1968); 27, 522 (1968).
148. H. L. Welsh and M. F. Crawford et al., Canad. J. Phys., 30, 577 (1952).
149. G. A. Vorob'eva, I. I. Kondilenko, and I. F. Klassen, Ukrain. Fiz. Zhur., 13, 193 (1968).
150. G. Eckhard and W. G. Wagner, J. Mol. Spectroscopy, 19, 407 (1966).
151. V. S. Ryazanov and M. M. Sushchinskii, Zhur. Eksper. Teor. Fiz., 54, 1099 (1968).
152. I. I. Kondilenko, P. A. Korotkov, and V. L. Strizhevskii, Optika i Spektrosk., 8, 470 (1960).
153. P. P. Shorygin and A. Kh. Khalilov, Zhur. Fiz. Khim., Zhur. Fiz. Khim., 25, 145 (1951).
154. H. W. Schrötter, Z. angew. Phys., 12, 275 (1960).
155. G. Michel and G. Duyckaerts, Spectrochim. Acta, 8, 356 (1957); 10, 257 (1958).
156. J. Brandmüller and H. Schrötter, Z. Physik, 149, 131 (1957).
157. D. A. Long, D. C. Milner, and A. G. Thomas, Proc. Roy. Soc., A237, 197 (1956).
158. Z. B. Alaune, Thesis, Vil'nyus, 1960.
159. N. K. Sidorov, L. S. Stal'makhova, et al., Optika i Spektrosk., 13, 783 (1962).
160. Kuak Dang Cheu, E. G. Treshchova, et al., Vestnik Moskov. Univ., Khimiya, No. 2, 20 (1968).
161. P. A. Akishin and V. M. Tatevskii, Vestnik Moskov. Univ., No. 2, 103 (1951); Dokl. Akad. Nauk SSSR, 76, 527 (1951).
162. T. Yoshino and H. J. Bernstein, J. Mol. Spectroscopy, 2, 213 (1958).
163. Yu. A. Lazarev and P. A. Bazhulin, Symposium, "Fizicheskie Problemy Spektroskopii" (Physical Problems in Spectroscopy), No. 2, Izd. Akad. Nauk SSSR, Moscow, 1963, p. 22.
164. E. Stansbury, M. F. Crawford, and H. L. Welsh, Canad. J. Phys., 34, 954 (1953).
165. Yu. A. Lazarev, Optika i Spektrosk., 17, 364 (1964).
166. T. Yoshino and H. J. Bernstein, Spectrochim. Acta, 14, 127 (1959).
167. N. I. Prokof'eva and L. M. Sverdlov, Optika i Spektrosk., 15, 315 (1963); 16, 370 (1964).
168. H. Schrötter and H. J. Bernstein, J. Mol. Spectroscopy, 12, 1 (1964); 22, 122 (1967).
169. M. G. Borisov and P. A. Bazhulin, Optika i Spektrosk., No. 2, 308 (1963).
170. P. A. Bazhulin, Yu. A. Lazarev, and N. V. Desyatova, Optika i Spektrosk., 13, 75 (1962).
171. D. A. Long and E. L. Thomas, Trans. Faraday Soc., 59, 1026 (1963).
172. D. N. Waters and L. A. Woodward, Proc. Roy. Soc., A246, 119 (1958).
173. K. A. Taylor and L. A. Woodward, Proc. Roy. Soc., A264, 558 (1961).
174. W. Holzer and H. Moser, J. Mol. Spectroscopy, 13, 430 (1964).
175. Z. Kecki and H. J. Bernstein, J. Mol. Spectroscopy, 15, 378 (1965); 22, 122 (1967).
176. L. A. Leites, Thesis, Moscow, 1965.
177. F. Perzl and H. Moser, J. Mol. Spectroscopy, 26, 237 (1968).
178. L. A. Woodward and D. A. Long, Trans. Faraday Soc., 45, 1131 (1949).
179. T. V. Long and R. A. Plane, J. Chem. Phys., 43, 457 (1965).
180. H. Stammreich and R. Forneris, J. Chem. Phys., 25, 1278 (1956).
181. A. Müller and B. Krebs, J. Mol. Spectroscopy, 24, 180, 198 (1967).
182. Ya. S. Bobovich, Optika i Spektrosk., 11, 161 (1961).
183. S. V. Markova and P. A. Bazhulin, Symposium, "Fizicheskie Problemy Spektroskopii" (Physical Problems in Spectroscopy), Vol. 1, Izd. Akad. Nauk SSSR, Moscow, 1962, p. 433.
184. H. L. Welsh, M. F. Crawford, and G. D. Scott, J. Chem. Phys., 16, 97 (1948).
185. G. W. Chantry and R. A. Plane, J. Chem. Phys., 32, 319 (1960); 34, 1268 (1961).

186. Yu. N. Sheinker and Ya. K. Syrkin, Izv. Akad. Nauk SSSR, Ser. Fiz., 14, 478 (1950).
187. G. W. Chantry and R. A. Plane, J. Chem. Phys., 35, 1027 (1961).
188. K. A. Taylor, T. V. Long and R. A. Plane, J. Chem. Phys., 47, 138 (1967).
189. M. V. Vol'kenshtein, M. A. El'yashevich, and B. I. Stepanov, "Kolebaniya Molekul" (Molecular Vibrations), Ch. 24, Izd. GTTI, Moscow, 1949.
190. E. R. Lippincott and G. Nagarajan, Bull. Soc. chim. belges, 74, 551 (1965).
191. E. R. Lippincott and J. M. Stutman, J. Phys. Chem., 68, 2926 (1964).
192. L. S. Mayants and B. S. Averbuch, J. Mol. Spectroscopy, 22, 197 (1967).
193. L. M. Sverdlov, Optika i Spektrosk., 17, 369 (1964).
194. D. A. Long, R. Gravenor, and D. Milner, Trans. Faraday Soc., 59, 46 (1963).
195. D. G. Rea, Analyt. Chem., 32, 1638 (1960).
196. Yu. P. Egorov, V. A. Khranovskii, et al., Teor. Eksper. Khim., 6, 90, 743 (1970).
197. V. T. Aleksanyan, Kh. E. Sterin, et al., Izv. Akad. Nauk SSSR, Ser. Fiz., 22, 1073 (1958).
198. H. Moser and U. Weber, "Advances in Molecular Spectroscopy", Pergamon, Oxford, 1962, p. 1116.
199. E. G. Treshchova, V. R. Skvarchenko, and R. Ya. Levina, Vestnik Moskov. Univ., Khimiya, No. 5, 66 (1962).
200. G. Michel, Bull. Soc. chim. belges, 68, 643 (1959); 72, 125 (1963).
201. E. V. Sobolev, V. T. Aleksanyan, et al., Zhur. Strukturnoi Khim., 2, 147 (1961).
202. Yu. P. Egorov, L. A. Leites, and V. F. Mironov, Zhur. Strukturnoi Khim., 2, 562 (1961).
203. M. F. Shostakovskii, N. I. Shergina, et al., Zhur. Obshch. Khim., 35, 1768 (1965).
204. M. F. Shostakovskii, N. I. Shergina, et al., Dokl. Akad. Nauk SSSR, 158, 1143 (1964).
205. V. M. Tatevskii, E. G. Treshchova, et al., Zhur. Fiz. Khim., 23, 657 (1949).
206. S. V. Markova and P. A. Bazhulin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1280 (1959).
207. L. A. Leites, I. D. Pavlova, and Yu. P. Egorov, Teor. Eksper. Khim., 1, 311 (1965).
208. E. G. Treshchova, V. M. Tatevskii, et al., Optika i Spektrosk., 10, 63 (1961).
209. G. V. Peregudov, S. V. Markova, et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 37 (1957).
210. M. M. Sushchinskii, Izv. Akad. Nauk SSSR, Ser. Fiz., 17, 608 (1953).
211. H. Kriegsmann, Pure Applied Chem., 13, 203 (1966).
212. P. Reich and H. Kriegsmann, Z. anorg. Chem., 334, 283 (1965).
213. P. A. Akishin, N. G. Rambidi, et al., "Sbornik Trudov Mezhvuzovskogo Soveshchaniya po Khimii Nefti" (Proceedings of the Intercollegiate Conference on Petroleum Chemistry), Izd. Moskov. Univ., 1960, p. 146.
214. P. A. Akishin and N. G. Rambidi, Dokl. Akad. Nauk SSSR, 102, 747 (1955).
215. M. V. Vol'kenshtein, Zhur. Fiz. Khim., 17, 62 (1943).
216. V. M. Tatevskii, Zhur. Fiz. Khim., 20, 129 (1946).
217. G. Allen and J. H. Bernstein, Canad. J. Chem., 32, 1124 (1954).
218. V. T. Aleksanyan, M. Yu. Lukina, S. V. Zotova, et al., Dokl. Akad. Nauk SSSR, 171, 95 (1966).
219. V. N. Vasil'eva, V. P. Bazov, and M. A. Geiderikh, Zhur. Fiz. Khim., 33, 1516 (1959).
220. P. P. Shorygin and Z. B. Alaune, Zhur. Fiz. Khim., 34, 2299 (1960).
221. S. S. Urazovskii and O. A. Gunder, Dokl. Akad. Nauk SSSR, 91, 885 (1953).
222. L. Z. Osityanskaya, Thesis, Moscow, 1955.
223. S. M. Shostakovskii, Ya. M. Kimel'fel'd, and A. V. Bobrov, "Khimiya Atsetilena" (Acetylene Chemistry), Izd. Nauka, Moscow, 1968, p. 267.
224. Ya. S. Bobovich, Optika i Spektrosk., 19, 279 (1965); 20, 252 (1966).
225. P. P. Shorygin, M. F. Shostakovskii, et al., Izd. Akad. Nauk SSSR, Otd. Khim. Nauk, 1571 (1961).
226. G. V. Ratovskii, V. V. Dorokhova, et al., Dokl. Akad. Nauk SSSR, 190, 1124 (1970).
227. Ya. S. Bobovich and V. V. Perekalin, Dokl. Akad. Nauk SSSR, 127, 1239 (1959).
228. Z. B. Alaune and Z. A. Talaikite, Trudy Akad. Nauk LitSSR, B2, 57 (1964).
229. M. Harrand and H. Martin, Bull. Soc. chim. France, 1383 (1956).
230. P. A. Akishin and V. M. Tatevskii, Dokl. Akad. Nauk SSSR, 89, 287 (1953).
231. P. P. Shorygin, M. A. Geiderikh, and T. Ambrush, Zhur. Fiz. Khim., 34, 335 (1960) [Russ. J. Phys. Chem., No. 2 (1960)].
232. P. P. Shorygin, V. P. Roshchupkin, and L. G. Stolyarova, Zhur. Fiz. Khim., 39, 605 (1965) [Russ. J. Phys. Chem., No. 3 (1965)].
233. J. C. Evans and H. J. Bernstein, Canad. J. Chem., 33, 1746 (1955).
234. Ya. M. Kimel'fel'd, V. T. Alaksanyan, et al., Zhur. Strukturnoi Khim., 7, 42 (1966).
235. P. P. Shorygin, V. P. Roshchupkin, et al., Zhur. Fiz. Khim., 35, 258 (1961) [Russ. J. Phys. Chem., No. 2 (1961)].
236. V. S. Kukina, S. M. Kats, and L. M. Sverdlov, Optika i Spektrosk., 23, 427, 550, 911 (1967); No. 3, 296 (1967).
237. P. P. Shorygin and Z. B. Alaune, Zhur. Fiz. Khim., 33, 717 (1959) [Russ. J. Phys. Chem., No. (1959)].
238. Yu. P. Egorov and R. A. Loktionova, Teor. Eksper. Khim., 1, 160 (1965).
239. Yu. L. Frolov, A. Kh. Fillipova, et al., Zhur. Strukturnoi Khim., 3, 676 (1962).
240. E. G. Treshchova, Yu. N. Panchenko, et al., Optika i Spektrosk., 8, 371 (1960).
241. Yu. S. Shabarov, T. P. Surikova, et al., Vestnik Moskov. Univ., Khimiya, No. 2, 79 (1967).
242. A. N. Nikitina, V. A. Petukhov, et al., Optika i Spektrosk., 16, 979 (1964).
243. R. Ya. Levina, P. A. Gembitskii, and E. G. Treshchova, Zhur. Obshch. Khim., 33, 365, 371 (1963).
244. P. P. Shorygin, V. A. Petukhov, et al., Zhur. Fiz. Khim., 42, 1057 (1968) [Russ. J. Phys. Chem., No. 5 (1968)].
245. P. P. Shorygin, V. A. Petukhov, et al., Zhur. Fiz. Khim., 42, 1584 (1968) [Russ. J. Phys. Chem., No. 5 (1968)].
246. A. E. Borisov, N. V. Novikov, et al., Ukrain. Fiz. Zhur., 13, 75 (1968).
247. E. M. Popov and G. A. Kogan, Optika i Spektrosk., 12, 194 (1962); 11, 730 (1961).
248. E. M. Popov and I. P. Yakovlev, Zhur. Strukturnoi Khim., 9, 54 (1968).
249. Yu. P. Egorov and G. G. Kirei, Zhur. Obshch. Khim., 34, 3615 (1964).

250. G. Peddle, J. Organometall. Chem., **14**, 115, 139 (1968).
251. H. D. Kaesz and F. G. Stone, Spectrochim. Acta, 360 (1959).
252. P. L. Goggin and L. A. Woodward, Trans. Faraday Soc., **62**, 1423 (1966).
253. L. N. Jones, Spectrochim. Acta, **19**, 1675 (1963).
254. E. N. Tsvetkov, D. A. Bochvar, and M. I. Kabachnik, Teor. Eksper. Khim., **3**, 3 (1967).
255. P. P. Shorygin, T. N. Shkurina, et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1011 (1961).
256. L. G. Vorontsova, Zhur. Strukturnoi Khim., **7**, 280 (1966).
257. P. P. Shorygin and Z. S. Egorowa, "Proceedings of the Fourth International Meeting on Molecular Spectroscopy", Bologna, **2**, 551 (1962).
258. S. M. van der Krogt and B. M. Wepster, Rec. Trav. chim., **74**, 161 (1953).
259. H. Pracejus and M. Kehlen, et al., Tetrahedron, **21**, 2257 (1965).
260. J. Degani and A. Mangini, et al., Spectrochim. Acta, **23A**, 1351 (1967).
261. P. A. Akishin, N. G. Rambidi, et al., Vestnik Moskov. Univ., No. 3, 77 (1954); No. 12, 103 (1955).
262. V. A. Shlyapochnikov and V. G. Osipov, Optika i Spektrosk., **20**, 917 (1966).
263. E. M. Popov and E. D. Lubuzh, Zhur. Prikl. Spektrosk., **5**, 498 (1966).
264. Yu. N. Panchenko and G. S. Koptev, Vestnik Moskov. Univ., Khimiya, No. 1, 44 (1968); No. 4, 39 (1969).
265. N. V. Tarasova and L. M. Sverdlov, Optika i Spektrosk., **18**, 587 (1965).
266. K. W. Kholrausch, Phys. Z., **37**, 58 (1936).
267. M. J. Dewar and G. J. Gleicher, J. Amer. Chem. Soc., 87, 692 (1965).
268. O. W. Adams and R. L. Miller, J. Amer. Chem. Soc., **88**, 404 (1966).
269. E. M. Popov, G. A. Kogan, and T. M. Ivanova, Zhur. Prikl. Spektrosk., **1**, 123 (1964).
270. M. V. Vol'kenshtein and S. M. Yazykova, Dokl. Akad. Nauk SSSR, **104**, 835 (1955).
271. F. A. Savin and I. I. Sobel'man, Optika i Spektrosk., 7, 733 (1959).
272. F. A. Savin, Optika i Spektrosk., 15, 42 (1963).
273. A. van Veen, P. E. Verkade, and B. M. Wepster, Rec. Trav. chim., **76**, 801 (1957).
274. B. M. Webster, "Steric Effects in Conjugated Systems", Butterworths, London, 1959, p. 82.
275. E. V. Sobolev, V. T. Aleksanyan, et al., Zhur. Strukturnoi Khim., **4**, 189, 354, 527 (1963).
276. S. V. Markova, P. A. Bazhulin, and M. M. Sushchinskii, Optika i Spektrosk., **1**, 41 (1956).
277. H. Junge, Spectrochim. Acta, **24A**, 1965 (1968).
278. K. Noack and R. N. Jones, Canad. J. Chem., **39**, 2201 (1961).
279. E. V. Sobolev and V. T. Aleksanyan, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1336 (1963).
280. V. T. Aleksanyan and Ya. M. Kimel'fel'd, Zhur. Prikl. Spektrosk., **3**, 355 (1965).
281. E. G. Treshchova, V. M. Tatevskii, et al., Optika i Spektrosk., **5**, 553 (1958).
282. M. M. Sushchinskii and V. I. Tyulin, Dokl. Akad. Nauk SSSR, **95**, 505 (1954).
283. A. E. Lutskii, A. K. Kul'chintskaya, et al., Zhur. Obshch. Khim., **36**, 1577 (1966).
284. M. R. Yagudaev, E. M. Popov, et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1189 (1964).
285. P. P. Shorygin and B. V. Lopatin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1371 (1967).
286. V. T. Aleksanyan, O. A. Shcherbakova, and A. F. Plate, Dokl. Akad. Nauk SSSR, **152**, 602 (1963).
287. R. Ya. Levina, V. N. Kostin, et al., Zhur. Obshch. Khim., **32**, 1377 (1962); **31**, 829 (1961).
288. A. L. Goodman and R. H. Eastman, J. Amer. Chem. Soc., **86**, 908 (1964).
289. J. Pete, Bull. Soc. chim. France, 357 (1967).
290. H. A. Bent, Chem. Rev., **61**, 275 (1961).
291. P. P. Shorygin, V. A. Petukhov, and L. G. Stolyarova, Dokl. Akad. Nauk SSSR, **154**, 441 (1964).
292. L. A. Leites, T. K. Gar, and V. F. Mironov, Dokl. Akad. Nauk SSSR, **158**, 400 (1964).
293. R. M. Roberts and F. Kaissi, J. Organometall. Chem., **12**, 79 (1968).
294. M. M. Kreevoy, P. J. Steinwand, and T. S. Straub, J. Org. Chem., **31**, 4291 (1966).
295. W. Musker, J. Organometall. Chem., **6**, 627 (1966).
296. V. S. Griffiths and G. A. Derwish, J. Mol. Spectroscopy, **7**, 233 (1961).
297. C. F. Wilcox and A. C. Craig, J. Org. Chem., **26**, 2491 (1961).
298. M. B. Robin and N. A. Kuebler, J. Chem. Phys., **44**, 2664 (1966).
299. H. E. Simmons and T. Fukunaga, J. Amer. Chem. Soc., **89**, 5208 (1967).
300. R. C. Cookson, Proc. Roy. Soc., **A297**, 27 (1967).
301. R. G. Kostyanovskii and O. A. Pan'shin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 564 (1965).
302. L. G. Vorontsova, V. I. Andrianov, and B. L. Tarnopol'skii, Zhur. Strukturnoi Khim., **10**, 872 (1969).
303. I. N. Juchnovski, Dokl. Bolg. Akad. Nauk, **20**, 97 (1967).
304. S. M. van der Krogt and B. M. Wepster, Rec. Trav. chim., **74**, 161 (1955).
305. M. Prochazka and M. Palecek, Chem. Listy, **61**, 298 (1967).
306. E. N. Prilezhaeva, N. P. Petukhova, et al., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2443 (1968).
307. G. V. Ratovskii, Yu. A. Frolov, et al., Izv. Vys. Ucheb. Zaved., Fiz., No. 1, 112 (1968).
308. Yu. L. Frolov, A. V. Kalabina, et al., Zhur. Strukturnoi Khim., **6**, 397 (1965).
309. C. G. Pitt and M. S. Fowler, J. Amer. Chem. Soc., **89**, 6792 (1967).
310. H. Gilman and W. H. Atwell, J. Organometall. Chem., **2**, 369 (1964).
311. H. Sakurai and M. Kumada, Bull. Chem. Soc. Japan, **37**, 1894 (1964).
312. H. Gilman and P. J. Morris, J. Organometall. Chem., **6**, 102 (1966).
313. D. N. Hague and R. H. Prince, Proc. Chem. Soc., 300 (1962).
314. P. P. Shorygin, V. P. Roshchupkin, and A. Kh. Khomenko, Dokl. Akad. Nauk SSSR, **159**, 391 (1964).
315. A. I. Finkel'shtein, Yu. A. Arbuzov, and P. P. Shorygin, Zhur. Fiz. Khim., **24**, 802 (1950).
316. Ya. S. Bobovich, E. S. Lipina, and V. V. Perekalin, Zhur. Strukturnoi Khim., **5**, 546 (1964).
317. G. I. Chipen, Ya. A. Eidus, and Ya. S. Bobovich, Zhur. Strukturnoi Khim., **6**, 53 (1965).
318. A. S. Sopova, V. V. Perekalin, and Ya. S. Bobovich, Zhur. Obshch. Khim., **31**, 1528 (1961).
319. E. Ziegler, Z. analyt. Chem., **213**, 9 (1965).
320. R. E. Hester and R. A. Plane, J. Chem. Phys., **45**, 4588 (1966).
321. A. V. Bobrov and Kh. E. Sterin, Optika i Spektrosk., **15**, 130 (1963).

322. K. Noack and R. N. Jones, Canad. J. Chem., 39, 2225 (1961).
323. S. Dzhessati, V. I. Tyulin, et al., Vestnik Moskov. Univ., Khimiya, No. 2, 14 (1967).
324. Ya. E. Eidus and I. V. Zuika, Izv. Akad. Nauk LatvSSR, Ser. Fiz., No. 2, 75 (1965).
325. J. Tang and A. C. Albrecht, J. Chem. Phys., 49, 1144 (1968).
326. I. V. Shevchenko, I. V. Kovalev, M. G. Voronkov, Yu. I. Khudobin, and N. P. Kharitonov, Zhur. Fiz. Khim., 44, 1898 (1970 [Russ. J. Phys. Chem., No. 8 (1970)].
327. C. G. Pitt, J. Organometall. Chem., 23, C35 (1970).
328. Ya. S. Bobovich and A. B. Bortkevich, Uspekhi. Fiz. Nauk, 103, 3 (1971).

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