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The study of the Raman effect has yielded much important information, useful both for chemistry and for physics. The study of the resonance Raman effect can contribute not only to the extension of the technique of Raman spectroscopy, but also to an investigation of the nature of the interaction of light with matter.

The Raman effect can be satisfactorily described and the principal parameters interpreted in terms of both the classical and the quantum theory.

In the classical theory, the intensity of the Raman line (I) is determined by the polarizability derivatives with respect to the normal nuclear co-ordinate q_m^* and by the amplitudes of the vibrations of the nuclei. The intensity of the fundamental (I_1) will depend on all the components of the tensor α' , and for the simple case will be equal to the square of the largest component.

In quantum theory, the intensity is expressed in terms of matrix elements of the polarizability α_{0n} , where 0 and n denote the initial and the final vibration quantum number.

As has been shown by Placzek, when the exciting frequency ν is far from an electronic absorption band of the molecule, ν_e , $\alpha' q_{01} = d_{02}$, where q_{01} is the Oth amplitude of nuclear vibrations. The polarizability derivative and α_{0n} are related to the parameters of the electronic excitation levels, which may be determined from the electronic absorption spectrum. The intensity I is related to ν not only by the presence of the ν^4 factor, but also due to the dependence upon ν of α' or α_{01} respectively.

The dependence of the polarizability of the molecule upon the nuclear co-ordinate is fairly complicated. It appears reasonable, therefore, to consider, on the basis of the simplest semi-classical theory, the dependence of separate terms in the polarizability formulae upon the co-ordinate q. Presented below are the results obtained by the author and L. L. Krushinskii1-3.

We shall assume that the polarizability is given by the expression:

$$\alpha = \frac{z^2}{4\pi^2 c^2 \mathrm{m}} \sum_{\epsilon} \frac{f_{\epsilon}}{v_{\epsilon}^2 - v^2 + i v \gamma_{\epsilon}} \tag{1}$$

where f_{ϵ} is the oscillator strength calculated from the absorption band area, ν_{e} is the frequency of the absorption band maximum in cm⁻¹, γ_{e} is the attentuation coefficient, z and m are the electron charge and mass respectively, and c is the velocity of light. The summation is made over all the electronic excitation levels e.

Equation (1), as well as all those derived from it, could be written for every Cartesian component of α , using the corresponding f_{ex} , f_{ey} or f_{ez} values.

^{*}The subscript m denoting normal vibration will be omitted hereafter. †The derivatives of polarizability (a) with respect to q are denoted hereafter by primes.

The f values may be replaced by the squares of matrix elements of dipole moment transition, $(M_{0\epsilon})^2$, constructed from total wave functions.

In order not to distract attention from our main point, we shall confine the present treatment to simplified expressions.

The polarizability derivative, $(\partial \alpha/\partial q)_0$, is to be found by differentiating equation (1), provided ν_e and f_e are the functions of the nuclear co-ordinate q (see Shorygin and Krushinskii²):

$$\alpha' = \frac{z^2}{4\pi^2 c^2 m} \sum \left[\frac{f_{e'}}{v_{e}^2 - v^2 + i \nu \gamma_e} - \frac{2f_{e} v_{e} v_{e'}^2}{(v_{e}^2 - v^2 + i \nu \gamma)_{e}^2} \right]$$
(2)

The second derivative, which is proportional to an overtone intensity (I_2) , is given by:

$$\alpha'' = \frac{z^2}{4\pi^2 c^2 m} \sum_{\epsilon} \left[\frac{f_{\epsilon''}^{\prime\prime}}{v_{\epsilon}^2 - v^2 + iv\gamma_{\epsilon}} - \frac{4f_{\epsilon}'v_{\epsilon}v_{\epsilon}' + 2f_{\epsilon}v_{\epsilon}v_{\epsilon}''}{(v_{\epsilon}^2 - v^2 + iv\gamma_{\epsilon})^2} + \frac{2f_{\epsilon}v_{\epsilon}'^2 (3v_{\epsilon}^2 + v^2 - iv\gamma_{\epsilon})}{(v_{\epsilon}^2 - v^2 + iv\gamma_{\epsilon})^3} \right]$$
(3)

The terms in the denominators including the attenuation coefficient may be neglected in equations (2) and (3) for regions beyond an absorption band.

Equation (2) replaces the dependence of the polarizability upon the co-ordinate, which guarantees production of the Raman effect, by the dependence of an electronic transition frequency and of an oscillator strength upon the co-ordinate. The dependence of M_{0s} upon q is considered to be linear in the first approximation:

$$M_{0e}(q) = (M_{0e})_0 (1 + \eta q)$$

where the coefficient η is most likely to be within the range of $\pm 2 \text{Å}^{-1}$.

The dependence of ν_e upon q can be estimated from the potential curve of an electronic excitation level E(q), particularly from its slope at the point corresponding to the nuclear equilibrium in the ground state, *i.e.* from the $(\delta\nu_e/\delta q)_0$. The slope increases with the increase in variations of the value of the mth normal nuclear co-ordinate, Δ_{em} , in the $0\rightarrow e$ electronic transition.

It will be noted that the greater the value of Δ_{em} , the greater will be the width of vibrational structure of an absorption band (corresponding to the mth normal vibration), and the greater will be the contribution of the corresponding electronic level e to the intensity of the Raman line⁵. The derivatives $(\delta v_e/\delta q)_0$ should be in the range from 0 to $-100,000~\rm cm^{-1}~\rm Å^{-1}$ in most cases. Typical potential energy curves E(q) for the ground and the excited electronic states are presented in Figure 1. The vertical arrow shows the incident light quantum, which is here much less than that absorbed by the molecule during the so-called Franck-Condon transition.

In the binomials summated in equation (2), either the first term containing f_{i} or the second containing ν_{i} could be dominant. If the terms are of different signs, they may partially or entirely compensate each other. The first terms are most likely to dominate when $\nu \ll \nu_{i}$, i.e. in regions remote from resonance. With the increase of ν_{i} , the second terms should increase more rapidly than the first ones, and they are likely to dominate under usual

conditions of excitation, especially when ν_{ϵ} is not great. This is confirmed by the following facts:

- (a) by the form of the $I = f(\nu)$ dependence;
- (b) by the presence in the Raman spectrum of normal vibrations which may be observed in the vibrational structure of an absorption band;

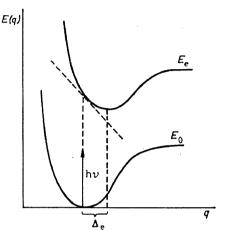


Figure 1. Typical potential energy curves illustrating the dependence of v_e upon q

(c) by the fact that the intensity of the lines of valence vibration depends on frequency to a greater extent than does the intensity of deformation vibrations.

The second terms should contribute much more to the dependence $I = f(\nu)$ than the first ones. Indeed, in the regions far from the resonance, where the first terms are more important, the factor ν^4 is dominant, and the dependence of α' upon ν can be neglected altogether; the dependence of α' is essential for regions near resonance, where second terms should dominate.

When the incident frequency ν is near to an absorption band and the second term is dominant, we will have instead of equation (2):

$$|\alpha'| = \frac{z^2 f_e \nu_e \nu'_e}{2\pi^2 c^2 \operatorname{m} \left[(\nu_e^2 - \nu^2)^2 + \nu^2 \gamma_e^2 \right]}$$
(4)

The intensity will depend on the square of modulus, $|\alpha'|^2$.

Placzek in his theory introduced the dependence of M_{0e} upon q only for regions near an absorption band; on the other hand, he supposed that factors equivalent to the "second term" of the semi-classical theory were altogether outside the scope of his "theory of the polarizability". However, the dependence of the polarizability upon the nuclear co-ordinate, and, therefore, the production of the Raman effect, is due to both terms for every region either near to or far from resonance.

Figure 2 illustrates equations (1) and (4). It presents the parameters of the classical model of a diatomic molecule with an attenuation constant which is of considerable size. The following values are brought together:

(a) the absorption curve, $\epsilon = f(\nu)$;

- (b) the real part of the polarizability, Re $\alpha(\nu)$;
- (c) vectors (broken arrows) representing the complex polarizability α on complex planes for a number of values of ν (each value shown by a vector origin on the frequency scale); the vector projection on the x-axis is the real part of the polarizability, and the projection on y-axis—the imaginary part (the vector of an incident wave field coincides with the x-axis);
- (d) vectors of complex derivatives of the polarizability (solid arrows) for the same values of the exciting frequency ν ; (α and α' are drawn on an arbitrary scale).

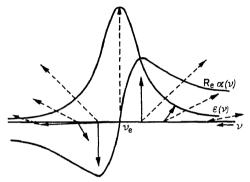


Figure 2. Complex values of α (broken arrows) of α' (solid arrows) for various regions of an absorption band

Values of α' are imaginary for the two ν values, limiting an absorption band half-width, and are real in the absorption band centre $(\nu \sim \nu_e)$ as well as in regions beyond an absorption band. The quantum model treatment yields similar results².

For regions beyond an absorption band, the Raman effect may be considered a result of amplitude modulation of an induced moment vibrations; in the centre of an absorption band the phase modulation is predominant. When the phase modulation is great, strong overtones are likely to appear.

Figure 3 represents complex polarizability values for the equilibrium (AB) vector) and for the two extreme values (AC) and AD of the vibrating nuclei co-ordinate in the case of resonance $(\nu \sim \nu_e)$. The DC vector corresponds to the double amplitude of the polarizability modulation, i.e. to $2\alpha'q_{01}$ or, more precisely, to the difference $(\Delta\alpha)$ of the two polarizability values corresponding to the two extreme positions of the nuclei. The intensity of the fundamental is represented to a closer approximation by this difference than by the polarizability derivative (i.e. $2\alpha'q_{01}$). The FB vector, which is the difference of the BC and DB vectors, corresponds approximately to the $\alpha''(q_{01})^2$ value and determines an overtone intensity, I_2 . In order to simplify the interpretation of Figure 3, it can be assumed (but only conditionally) that ν , and not ν_e , is changing with the nuclear vibrations².

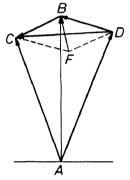
When the attenuation constant γ_e is great (much greater than the nuclear vibration frequency ω), the simplest classical model and the corresponding $|\alpha'|q_{01}$ may be used to describe the Raman effect for regions both beyond and inside an absorption band. In the case of a smaller attenuation constant, the model may be applied only when the frequency ν is located beyond an

absorption band. The treatment can be somewhat extended, however, in the latter case, should the contribution of higher polarizability derivatives be taken into consideration. Then, instead of one term containing α' , we shall have the series:

$$\alpha' q_{01} + b \alpha''' q_{01}^3 + c \alpha''''' q_{01}^5 + \dots$$

For the simple classical model, b=1/8, c=1/192. If the more correct expression $\int u_0\alpha(q)u_1\mathrm{d}q$ is used, where u_0 and u_1 are the nuclear wave functions, then b=1/2 and c=1/8. The presence of higher derivatives deprives the classical formulae of the simplicity which is the main advantage of the classical model. The contribution of higher derivatives may be included in more compact form, though incompletely (with the coefficients b=1/6 and c=1/120), if the intensity is taken to be proportional, not to $a'q_{01}$, but to the difference of the two polarizability values corresponding to the extreme positions of the vibrating nuclei.

Figure 3. Complex values of the polarizability of a molecule for equilibrium (AB) and for two extreme positions (AC) and (AD) of vibrating nuclei



Further improvement can be made if the influence of the vibration frequency ω , and of the attenuation constant γ_e , on the modulations of the induced moment vibrations is taken into account. This can be done by introducing a factor dependent on γ/ω .

The model considered above, though imperfect, may be used not only for qualitative, but in some cases even for quantitative description. For the further development of the classical theory, the more general solution of the equation for electron motion* is to be found:

$$\ddot{\chi} + \gamma \dot{\chi} + v_0^2 \left[1 + f(\omega t)\right]^2 \chi = k \cos \nu t$$

where χ is an electron co-ordinate the quantum theory of the Raman effect is based upon the Kramers-Heisenberg-Weisskopf equation, which includes the contributions of every electronic level e, and every corresponding vibrational sublevel v. By separating the nuclear and the electronic wave functions in the Born-Oppenheimer approximation, we obtain^{1,2}:

$$\alpha_{0n} = \frac{2}{hc} \sum_{e} \sum_{v} \frac{v_{ev}}{v_{ev}^2 - v^2 + iv\gamma_{ev}} (M_{0e})^2 A_{0v} A_{vn}$$
 (5)

^{*}Frequency is expressed here in rad/sec.

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where ν_{ev} is the frequency of an electronic-vibrational transition $0, 0 \rightarrow e, v, M_{0e}$ is the matrix element of a dipole moment transition $0 \rightarrow e$, constructed from electronic wave functions, and A_{0v} the overlap integral for nuclear functions, $\int u_{v}^{(0)}(q) u_{v}^{(e)}(q) dq$ (the subscript and the superscript denoting vibrational and electronic quantum number respectively).

Written in this form, the equation can be readily analysed, since its parameters could be either calculated or at least evaluated. The equation illustrates the contribution of vibrational sub-levels, and also the meaning of the imaginary and the real part of α_{0n} . It will be noted that the expression for a Raman line intensity should include $|\alpha_{0n}|$

For regions beyond an absorption band the imaginary part of α_{0n} could be neglected in equation (5). This cannot be done for regions inside the band, but, in this case, one may confine the treatment to the contribution from only one electronic level, and, moreover, M_{0e} could be considered to be independent of q (or of v) and placed before the sum:

$$|\alpha_{01}| = \frac{2}{hc} (M_{0e})^2 \left| \sum_{v_{ev}} \frac{v_{ev}}{v_{ev}^2 - v^2 + iv\gamma_{ev}} A_{0v} A_{v1} \right|$$
 (6)

Figure 4 illustrates equation (5). It represents qualitatively the contribution of various vibration sublevels of an electronic excitation level to the α_{00} , α_{01} , and α_{02} values for a non-resonance case $(\nu \ll \nu_e)$. This is done for a molecular model, similar to that presented in Figure 2, in classical terms. I should like to remind the reader that α_{02} defines the first overtone intensity, I_2 . Vectors to the right and to the left of the vertical line represent the

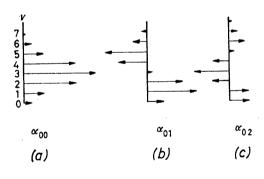


Figure 4. The contributions of vibration sub-levels of an electronic excitation level to the matrix elements of the polarizibility (α_{00} , α_{01} and α_{02}) when the exciting frequency is far from the resonance

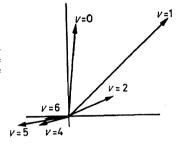
positive and negative contributions of sub-levels (quantum numbers v vary from 0 to 7). Since, in this case, ν is located beyond an absorption band, these contributions will not contain the imaginary part. The so-called Franck-Condon transition (in which the nuclear co-ordinate does not change) corresponds here to v=3. As seen from Figure 4, the absolute contribution of the latter to α_{01} is about zero, whilst it is greatest to α_{02} (Krushinskii and Shorygin³).

Figure 5 represents conditions near to resonance for the same model (γ_e) is large). Here the vectors on a complex plane correspond to the contributions of the same sub-levels to α_{01} .

Now we will compare the parameters of the classical and the quantum

models. At first sight they appear to be hardly comparable; thus, the powers in the resonance denominators in the classical formula (equation (2)) are considerably higher. However, the resonance denominators in equation (5) do not determine the dependence of α_{0n} upon ν immediately. The fact is that, in the "classical" equation (2), the summation is made only over electronic levels, whilst in the quantum formula it is also made over all

Figure 5. The complex contributions of vibration sublevels of an electronic level to the matrix element of the polarizability α_{01} near to resonance (when the lifetime of the excited state is small)



vibration sub-levels v of electronic excitation levels. Overlap integrals A_{v1} in equation (5), and, therefore, the corresponding contributions of sub-levels v of an electronic level to α_{01} , will have different signs, so that $\Sigma A_{0v}A_{v1}=0$ (Shorygin¹)*. For $v \leqslant v_e$, the resonance denominators corresponding to various sub-levels v do not differ greatly, and the contributions of the sub-levels could compensate each other, so that the sum will be about zero. With the increase of v, the degree of compensation lessens, the sum of the contributions increasing more rapidly than the absolute value of a separate contribution⁵. Thus, when v is not too close to v_e , i.e. in cases beyond an absorption band, the classical and the quantum formulae yield practically the same intensity values and the same dependence of the intensity upon the frequency, the classical formula being more simple.

The presence of the second term in the classical formula (the dependence of ν_e upon q) corresponds to the fact that resonance denominators are different for various sub-levels in the quantum formula. The introduction in equation (2) of the first term (the dependence of f_e upon q) corresponds to the inclusion of some variation in M_{0e} values for various sub-levels in the quantum theory. The introduction of some additional indices v for M_{0e} could provide for these variations; as the latter are not great, they could be neglected in most cases, especially when ν is not far from resonance.

The agreement between the classical and quantum model parameters is to be perceived in the following: the contributions (A_1) of vibrational sub-levels, located below the Franck-Condon level, to the matrix element of the polarizability α_{01} is proportional to the polarizability value (α_1) for one extreme position of the vibrating nuclei (q_{01}) , whereas the contribution $(-A_2)$, opposite in sign, of upper sub-levels is proportional to the polarizability value (α_2) for another extreme position $(-q_{01})$. The sum of the contributions of all sub-levels is: $A_1 - A_2 \sim \frac{1}{2}(\alpha_1 - \alpha_2)$.

As can be seen from equations (2)-(5), the Raman line intensities I_1 and I_2 should increase with increase of ν in the "before resonance" region ($\nu < \nu_e$),

^{*}Accordingly $\sum_{n} A_{0v} A_{v_r} = 0$ (see Krushinskii and Shorygin³ and Behringer⁶).

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and then decrease with further increase of ν (when ν ν_{e}). This has been confirmed by experiment. It should be noted that the position of the intensity maximum may be slightly different from that of the absorption coefficient maximum.

In the Raman spectrum of a compound the relation $I = f(\nu)$, even when determined by one electronic excitation level, may vary considerably from line to line. This could be caused by differences in the relative values of the first and second terms in the binomials of equation (2). The intensity of the lines of valence vibrations, when approaching resonance, should, in most cases, increase more rapidly than that of lines of deformation vibrations.

As to the rate at which the intensity increases as ν approaches an absorption band, it is moderate for I_1 and is slightly faster for I_2 when the attenuation constant is large. Even in the case of resonance, however, an overtone intensity should be much less than that of a fundamental $(I_2 \ll I_1)$, especially when Δ , a change in equilibrium value of the normal nuclear co-ordinate during electronic excitation, is small.

When the attenuation constant is not too large, I_1 increases rapidly as resonance is approached, while I_2 increases much faster, so that for true resonance I_2/I_1 is much greater than that in the previous case (for which γ is large).

Thus, in the resonance region, the overtone intensity should increase with a decrease in the attenuation constant more rapidly than the intensity of the fundamental, so that they may turn out to be of the same order. The intensity distribution, therefore, tends to that which would be observed in resonance fluorescence.

When the absorption band contour is caused primarily by the attenuation, the difference between the polarizability for two extreme nuclear positions, $\mid \Delta\alpha \mid$, should not exceed $0.001 \times \epsilon_{max}$. For p-nitro-N,N-diethylaniline $0.001 \times \epsilon_{max} = 25 \text{ Å}^3$. As evaluated from the intensity of the line of the nitro group in the case of resonance, $\mid \Delta\alpha \mid$ proved to be of the order of 50 Å^3 . Thus the attenuation cannot be considered a dominant factor, and γ_e should be considerably less than 4000 cm^{-1} .

For some nitro-compounds, the author and Ivanova⁷ have observed the narrow lines of the resonance Raman spectrum and the broad band of fluorescence simultaneously.

Presented in Figure 6 are the absorption spectrum (broken line) and the energy distribution in the emission spectrum (solid line) for 4-nitro-4'-dimethylaminostilbene. Crosses mark the Raman lines of the compound and of the solvent. 1340 is the line of the nitro-group; the arrow refers to the exciting mercury line (22938 cm⁻¹).

Study of the I = f(v) dependence has shown that both the Raman spectrum and fluorescence are connected with the same electronic excitation level. The mean lifetime of the excited state τ , as measured from the fluorescence after-glow, was about 10^{-9} sec. This value, however, is to be attributed primarily to the lowest vibrational sub-level of the electronic excitation level. The higher sub-levels, with a considerably shorter lifetime (probably of the order of 10^{-10} to 10^{-13} sec), should account for the Raman effect. However, should the resonance spectrum be a result of two subsequent acts of absorption and of emission, even such lifetime values, when a compound is in

liquid state, would have been enough for lines to undergo considerable broadening.

Since Raman lines remain narrow, they should be related to forced vibrations (when $\gamma_{vv} < \omega$, such a classification is somewhat conventional).

The resonance emission spectrum will depend on the relations of the following factors:

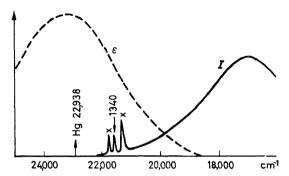


Figure 6. Energy distribution in the emission spectrum of 4-nitro-4'-dimethylaminostilbene

- (a) the half-width of the exciting band, Γ ;
- (b) the half-width of the vibration bands of the electronic excitation level, γ_{ev} ;
 - (c) The nuclear vibration frequency, ω .

When $\gamma_{ev} > \omega > \Gamma$, the resonance Raman spectrum which occurs corresponds to a "stationary process" and is described by equation (2).

When $\omega > \gamma_{ev} > \Gamma$, the observed Raman spectrum corresponds to a "non-stationary process", and the intensity of a line is less than that given by equation (2) (the discrepancies will increase as γ/ω decreases; the phase of the modulation of the induced moment vibrations should be retarded with respect to that of the nuclear vibrations.

When $\gamma_{ev} < \Gamma$, resonance fluorescence occurs.

The resonance Raman effect differs from resonance fluorescence by:

- (a) comparatively small vibration energy in the final state (low intensities of overtones);
 - (b) independence of the band-width upon γ_{ev} ;
- (c) insignificant after-glow, and insignificant influence of the molecular rotation on the depolarization ratio; low quantum yield; small influence of intermolecular interaction on the band-width;
- (d) dependence of the frequency of an emission line upon the exciting frequency.

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