

ON THE OCCURRENCE OF OVERTONE LINES IN RAMAN EFFECT

BY S. BHAGAVANTAM

(From the Department of Physics, Andhra University, Waltair)

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1. Harmonic Oscillator

THE theory of vibrational Raman scattering has been developed by a number of earlier workers and it is now generally recognised that the overtone lines, if at all they occur in Raman spectra, should ordinarily be very weak.* Placzek's work¹ contains a complete account of these and other important features relating to vibrational Raman lines. The relevant steps in the theory will be briefly given here. The polarisability of a molecule may be expanded as a series in the following manner:—

$$a(q) = a_0 + \sum_j \left(\frac{\partial a}{\partial q_j} \right)_0 q_j + \frac{1}{2} \sum_{jk} \left(\frac{\partial^2 a}{\partial q_j \partial q_k} \right)_0 q_j q_k + \dots \quad (1)$$

One special feature of this series is that only the limiting values of the derivatives pertaining to $q \rightarrow 0$ appear as the coefficients. The second and higher order derivatives under these conditions are likely to be quite negligible and the series may ordinarily be regarded as terminating with the second term. The q 's are the normal co-ordinates and they are so chosen that each one of them is zero when the molecule is in its equilibrium configuration. A set of values for the q 's will define a configuration q of the molecule. The matrix element $a_{\tau\tau'}$ will be given by (2)

$$a_{\tau\tau'} = \int \psi_{\tau'}^*(q) a(q) \psi_{\tau}(q) dq. \quad (2)$$

Let us, for simplicity, confine ourselves to diatomic molecules although results similar to those set forth below may easily be obtained for polyatomic molecules also. In such a case, there is only one degree of vibrational freedom to be considered and the change in the nuclear distance measured from the equilibrium value may be taken to represent the corresponding normal co-ordinate. If the molecule in question is regarded

* This statement does not apply to cases where overtones occur with unusually large intensities as a result of what has been termed 'accidental degeneracy'.

¹ *Handbuch der Radiologie*, 1934, 6, 205.

as an ideal harmonic oscillator, the ψ 's in (2) are real and represent the well-known eigen-functions of a harmonic oscillator involving the Hermite polynomials. Substituting the series (1) for $\alpha(q)$ in (2), the integration for specific values of ν and ν' may easily be performed by making use of the known properties of the Hermite polynomials. We have

$$\alpha_{01} = c^{\frac{1}{2}} \left(\frac{\partial \alpha}{\partial q} \right)_0; \quad \alpha_{02} = \frac{c}{\sqrt{2}} \left(\frac{\partial^2 \alpha}{\partial q^2} \right)_0, \quad (3)$$

where $c = h/8\pi^2\nu_0\mu$, μ is the reduced mass and ν_0 is the vibration frequency. In (3), only the first term has been retained in each of the cases and the others are omitted as they are relatively insignificant. The squares of α_{01} and α_{02} will respectively determine the intensities of the fundamental and the overtone. If, as has been explained in the beginning, the second order derivative of the polarisability is zero or negligibly small, the overtone line will be of either zero or negligibly low intensity. It is the purpose of the present paper to show that on the contrary, even if the series in (1) terminates with the second term, we should expect the overtone line to occur with a finite intensity on account of the fact that all diatomic molecules are in reality anharmonic oscillators. If we take this fact into account, it may easily be shown that a term involving the first derivative $\left(\frac{\partial \alpha}{\partial q} \right)_0$ also is present in the expression for α_{02} .

2. Anharmonic Oscillator

It has been shown by Morse² that the nuclear potential energy of various molecules is more satisfactorily represented by (4) than by the simple law appropriate to a harmonic oscillator

$$U(r) = D \{ e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \}. \quad (4)$$

r_0 is the equilibrium nuclear distance and r is a particular value. This leads to the eigen-values

$$E_n = h\nu_0 \left(n + \frac{1}{2} \right) - h\nu_0 x \left(n + \frac{1}{2} \right)^2.$$

The corresponding eigen-functions are no longer functions of Hermite polynomials but they involve the generalized Laguerre polynomials. If the radial part of the eigen-function is written as $1/r R_n(r)$, we have³

$$R_n(r) = A_n e^{-(k/2)e^{-a(r-r_0)}} [ke^{-a(r-r_0)}]^{\frac{(k-2n-1)}{2}} \cdot L_{kn}(ke^{-a(r-r_0)}) \quad (5)$$

² E. U. Condon and P. M. Morse, *Quantum Mechanics*, 1929,

³ J. L. Dunham, *Phys. Rev.*, 1929, **34**, 438,

where $K = 4\pi (2\mu D)^{\frac{1}{2}}/ah$ and $L_{kn}(ke - a(r - r_0))$ is a polynomial in $(ke - a(r - r_0))$ defined by

$$L_{kn}(x) = x^n - n(k - n - 1)x^{n-1} + \frac{1}{2}n(n-1)(k - n - 1)(k - n - 2)x^{n-2}.$$

A_n is given by

$$A_n = \left[\frac{a(k - 2n - 1)}{n!(k - n - 1)\Gamma(k - n - 1)} \right]^{\frac{1}{2}}.$$

The constants a and k are given by

$$a = (8\pi^2 \mu \nu_0 x/h)^{\frac{1}{2}}; \quad k = \frac{1}{x}.$$

The matrix element $\alpha_{zv'}$ will now be given by (6)

$$\alpha_{zv'} = \int R_{v'} a(q) R_v dr. \quad (6)$$

Regarding the series (1) as terminating with the second term only and substituting for $a(q)$, we have since $dr = dq$

$$\alpha_{01} = \left(\frac{\partial \alpha}{\partial q} \right)_0 \int R_1 R_0 q dq; \quad \alpha_{02} = \left(\frac{\partial \alpha}{\partial q} \right)_0 \int R_2 R_0 q dq. \quad (7)$$

A method of evaluating these integrals has been given by Dunham.³ Adopting the same procedure, we obtain

$$\begin{aligned} \alpha_{01} &= \left(\frac{\partial \alpha}{\partial q} \right)_0 \cdot \frac{A_0 A_1}{a^2} \Gamma(k - 1) \left\{ \log k - \frac{k}{1\frac{1}{2}} - \log k - \frac{k}{2\frac{1}{2}} \right\} \\ \alpha_{02} &= \left(\frac{\partial \alpha}{\partial q} \right)_0 \cdot \frac{A_0 A_2}{a^2} \Gamma(k - 1) \left\{ \log k - \frac{k}{1\frac{1}{2}} - 2 \frac{k - 3}{k - 2} \log k - \frac{k}{2\frac{1}{2}} \right. \\ &\quad \left. + \frac{k - 4}{k - 2} \log k - \frac{k}{3\frac{1}{2}} \right\}. \end{aligned} \quad (8)$$

A further simplification by substituting the values of A_0 , A_1 and A_2 in (8) will lead to (9)

$$\begin{aligned} \alpha_{01} &= \left(\frac{\partial \alpha}{\partial q} \right)_0 \cdot \frac{(k - 3)^{\frac{1}{2}}}{a} \left[\log k - \frac{k}{1\frac{1}{2}} - \log k - \frac{k}{2\frac{1}{2}} \right] \\ \alpha_{02} &= \left(\frac{\partial \alpha}{\partial q} \right)_0 \cdot \frac{[(k - 5)(k - 2)]^{\frac{1}{2}}}{\sqrt{2} \cdot a} \left[\log k - \frac{k}{1\frac{1}{2}} - 2 \frac{k - 3}{k - 2} \log k - \frac{k}{2\frac{1}{2}} \right. \\ &\quad \left. + \frac{k - 4}{k - 2} \log k - \frac{k}{3\frac{1}{2}} \right]. \end{aligned} \quad (9)$$

Thus we see that α_{02} survives even if the second order derivative of the polarisability with respect to the normal co-ordinate does not exist. In order to calculate the relative intensities of the fundamental and overtone Raman lines, it is only necessary to substitute the numerical values of a and k in (9) and obtain the squares of α_{01} and α_{02} . The results so

obtained in the case of a few common molecules are given in the next section. It may be remarked here that if the anharmonicity constant α is very small, k is very large and (9) reduces in the limit to (10).

$$\alpha_{01} = \frac{1}{a k^{\frac{1}{2}}} \left(\frac{\partial \alpha}{\partial q} \right)_0 ; \alpha_{02} = 0. \quad (10)$$

As may be expected, these agree with the values directly derived for an ideal harmonic oscillator on the assumption that the third and the higher terms in (1) are absent.

3. Application to Some Common Molecules

Taking the known spectroscopic constants,⁴ α_{01} and α_{02} have been calculated and given in Table I for some simple cases of diatomic molecules. The intensities of the corresponding Raman lines are in the ratio of $\nu_f^4 \alpha_{01}^2 : \nu_h^4 \alpha_{02}^2$, where ν_f and ν_h are respectively the frequencies of the fundamental and overtone Raman lines. These depend to some extent on the position of the exciting line and the figures given in the last column of Table I have been obtained on the assumption that the fundamental as well as the overtone line under comparison are excited by λ 3650 A.U.

TABLE I

Molecule	$\mu \times 10^{24}$	$\nu_0 x^\dagger$ (cm. ⁻¹)	ν_0^\dagger (cm. ⁻¹)	K	$a \times 10^{-8}$	$\alpha_{01} \times 10^{10}$	$\alpha_{02} \times 10^{11}$	$\frac{\alpha_{01}^2}{\alpha_{02}^2}$	$\frac{\nu_f^4 \times \alpha_{01}^2}{\nu_h^4 \times \alpha_{02}^2}$
HCl ..	1.615	51.90	2939.7	57.605	1.741	7.63	7.23	111	180
HBr ..	1.641	44	2647.0	60.16	1.616	8.04	7.46	116	176
H ₂ ..	0.831	113.5	4371.0	38.511	1.847	8.83	10.3	74	155
N ₂ ..	11.54	14.445	2359.6	163.35	2.455	3.19	1.77	325	478
O ₂ ..	13.19	11.645	1584.9	136.10	2.354	3.65	2.23	268	342

† The proper value to be used in calculating a is obtained by multiplying the figure in this column by the velocity of light.

It will be noted that the intensity of the fundamental is about 150 to 500 times that of the overtone in the set of molecules studied. This is an upper limit as we have assumed that $\left(\frac{\partial^2 \alpha}{\partial q^2} \right)_0$ does not exist. In a case where this term also exists, the overtone will have a larger intensity. Intense exposures with a view to record the overtone lines and check the theory of anharmonic oscillators have not so far been given. The case of

⁴ W. Jevons, *Report on Band Spectra of Diatomic Molecules*, 1932.

hydrogen is particularly encouraging and it should be quite possible to record the overtone at approximately double the normal Raman shift as its intensity is expected to be only $\frac{1}{155}$ of that of the fundamental.

It is possible to extend these ideas in a semi-empirical manner to more complicated molecules in order to explain the occurrence of overtone lines in their Raman spectra. This work along with a fuller discussion of the available experimental results in such cases will be taken up in a separate communication.