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ANHARMONICITY OF VIBRATION IN MOLECULES

BY K. S. VISWANATHAN

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1. INTRODUCTION

ANHARMONICITY of vibration is responsible for several of the finer features observed in the vibration spectra of molecules, *viz.*, the uneven spacing of the overtone levels of the different normal modes and the splitting of levels that are degenerate in the harmonic oscillator approximation. The spectrum of the vibrational energy levels, when the effect of anharmonic terms in the potential energy of the molecule is taken into account, has been the subject of several investigations, references to which can be had from the well-known books on the subject by Herzberg[1] and by Wilson, Decius and Cross.[2] In a detailed and elaborate piece of work, Nielson[3] has considered the problem for a general molecule taking account of one more complication, *viz.*, the vibration-rotation interaction in the molecule.

In the harmonic oscillator approximation, the normal modes of vibration of the molecule are independent of each other and the energy of the system is the sum of the energies of the $(3n - 6)$ normal modes of the molecule. When anharmonicity is taken into account, product terms of the third and higher powers in the normal co-ordinates are introduced in the potential energy of the system, and as a consequence the normal modes are no longer independent but interact with each other. The standard procedure for obtaining the corrections to the energy levels due to the anharmonic terms is by the perturbation method applied to $N = (3n - 6)$ variables and the results of the theory indicate that the energy levels get altered by the introduction of additional quadratic terms in the vibrational quantum numbers of the normal modes of the molecule. In the present paper, we adopt a different method and follow a procedure well known in the treatment of electronic motion in atoms and molecules, namely the method of the self-consistent field proposed by Hartree. Each normal mode of the molecule is assumed to be moving in the average potential field of vibration of the remaining ones, and the eigenfunctions and energy levels of each of the normal modes are calculated accordingly. Apart from the academic interest of the fact that the Hartree method can be applied to the problems of vibrational motion of the molecule, the procedure deserves attention

since it enables one to regard a molecule as an assembly of anharmonic oscillators and calculate the anharmonicity constants in terms of the force constants of the molecule, and also because it enables one to evaluate a measure of the interaction exerted on each mode by the remaining ones. Thus it is shown in Section 2 that a normal mode of the anti-symmetric species does not interact with the rest even in the first order of approximation. In Section 3, the question of degeneracy has been considered and eigen-functions and energy values for the case in which one of the modes is doubly degenerate have been evaluated.

2. THE ENERGY LEVELS

We start from the equilibrium configuration of the molecule, that is the configuration in which the forces acting on each atom of the molecule is zero. Referred to this state, the potential energy of the system will not contain any terms linear in the displacements of the atoms. If further we use normal co-ordinates, the potential and kinetic energies will not contain any quadratic cross terms and we can write therefore

$$T = \tfrac{1}{2} \sum_{i=1}^{N} \eta_i^2 \tag{1}$$

$$V = \tfrac{1}{2} \sum_{i=1}^{N} \lambda_i \eta_i^2 + \frac{1}{3!} \sum_i \sum_j \sum_k a_{ijk}\, \eta_i \eta_j \eta_k + \frac{1}{4!} \sum_i \sum_j \sum_k \sum_l \beta_{ijkl}\, \eta_i \eta_j \eta_k \eta_l \tag{2}$$

where $\eta_1, \eta_2, \ldots\ldots \eta_N$ ($N = 3n - 6$ or $3n - 5$ as the case may be) are the normal co-ordinates of the system. We first consider the case in which the system is non-degenerate. The constants $\lambda_1, \lambda_2, \ldots\ldots \lambda_N$ in (2) are then all different.

The wave function $\psi(\eta_1 \ldots \eta_N)$ describing the state of the molecule is given by the solution of the variational principle

$$\delta[J] = \delta \int \psi^* H \psi dV = 0 \tag{3}$$

subject to the condition

$$\int \psi^* \psi dV = 1 \tag{4}$$

where

$$H = (T + V) \quad \text{and} \quad dV = \prod_{i=1}^{N} d\eta_i.$$

We now try to approximate ψ in terms of the ' one normal co-ordinate ' wave functions $\psi_i(\eta_i)$, each of which depending on one normal co-ordinate only. We set

$$\psi = \psi_{v_1}(\eta_1)\,\psi_{v_2}(\eta_2)\ldots\ldots\ldots\psi_{v_N}(\eta_N) \tag{5}$$

where $v_1, v_2 \ldots\ldots\ldots v_N$ are integral numbers denoting the degree of excitation of the different normal modes, each moving in the field of the rest. The functions $\psi_{v_i}(\eta_i)$ are all assumed to be normalised, and the best possible choice of these which approximate the physical system as closely as possible are obtained as the solution of the variational principle (3). This leads to the following set of differential equations which the ψ's must satisfy.[4]

$$(H_i - \epsilon_i)\,\psi_{v_i} = 0 \tag{6}$$

where

$$H_i = \int \Big(\prod_{k\neq i} \psi_{v_k}^*\Big)\, H \Big(\prod_{k\neq i} \psi_{v_k}\Big) \prod_{k\neq i} d\eta_k \tag{7}$$

ϵ_i is independent of the suffix i and denotes the energy of the whole molecule.

To evaluate the Hamiltonian of the i-th normal mode as well as to determine its eigenfunction, we adopt the procedure of variation-iteration. To a first approximation, we ignore the quartic terms in (2) and substitute for all the wave functions $\psi_{v_k}(\eta_k)\,(k \neq i)$ in (7) the harmonic oscillator eigenfunctions of these normal co-ordinates. The integrals that arise in this process, like $\int \psi^*_{v_k}\,\eta_k^2\psi_{v_k}d\eta_k$ have been tabulated in Wilson's[2] book and making use of these, we find that equation (6) reduces to

$$\Big\{-\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial\eta_i^2} + (A_{i0}^{(1)} - \epsilon_i^{(1)}) + A_{i1}^{(1)}\eta_i + A_{i2}^{(1)}\,\eta_i^2 + A_{i3}^{(1)}\eta_i^3\Big\}\,\psi_{v_i}(\eta_i) = 0 \tag{8}$$

where

$$A_{i0}^{(1)} = \sum_{l\neq i}(v_l + \tfrac{1}{2})\,h\nu_l;$$

$$A_{i1}^{(1)} = \tfrac{1}{2}\sum_{m\neq i}\frac{a_{mmi}\,(v_m + \frac{1}{2})}{\gamma_m};$$

$$A_{i2}^{(1)} = \frac{\lambda_i}{2};$$

$$A_{i3}^{(1)} = \tfrac{1}{6}\, a_{iii};\ \text{and}$$

$$\gamma_m = \frac{4\pi^2 \nu_m}{h}. \tag{9}$$

The upper suffix in the above indicates the order of approximation.

Further $\epsilon_i^{(1)} = \int (\Pi \psi^*_{v_i})\, \mathrm{H}\, (\Pi \psi_{v_i}) \Pi\, d\eta_i$ and by substitution of the harmonic oscillator wave-functions in this we get

$$\epsilon_i^{(1)} = \sum_{l=1}^{N} (v_l + \tfrac{1}{2})\, h\nu_l.$$

Hence the eigenvalue of the i-th mode (*i.e.*) $(\epsilon_i^{(1)} - A_0^{(1)})$, is equal to $(v_i + \frac{1}{2})\, h\nu_i$. The first order approximation therfore does not introduce any corrections to the eigenvalues of the different normal modes from their harmonic oscillator values.

From (8) it follows that the Hamiltonian of the oscillator contains an anharmonic cubic term whose coefficient is the same as the coefficient of η_i^3 in the potential energy of the molecule and also a term linear in η_i. The linear term arises out of the process of averaging terms of the type $\eta_i \eta_l^2$ and it gives a measure of the action exerted by the other normal modes on the i-th one. It further suggests that the vibrations of the remaining modes tend to displace the equilibrium position of the i-th one from the place it occupies in the equilibrium configuration of the molecule as a whole.

The coefficient of the linear term is much smaller than the coefficient of the cubic one and their ratio is of the order of $1/\gamma \sim 10^{-16}$. But since the region wherein the displacement of the oscillator has a finite probability is of the order of $\gamma^{-\frac{1}{2}}$, both these terms are of the same order of smallness.

If the i-th mode belongs to an antisymmetric species of vibration of the molecule, all the coefficients of the type a_{mmi} and a_{iii} should be equal to zero. This is because the potential energy, including third and higher order terms, should be invariant under all the symmetry operations of the molecule and there will be at least one operation which will change the sign of a normal co-ordinate falling under an antisymmetric species of the molecule. Thus from (9) it follows that *to a first approximation a normal mode belonging to the antisymmetric species of vibration of the molecule does not interact with the rest and also it suffers no anharmonicity.*

The first order eigenfunctions of (8) may be obtained by the perturbation method. The normalised eigenfunctions are given by

$$\psi_{v_i}^{(1)} = a_i \psi_{v_i}^{(0)} + a_{i-3}^{(0)} \psi_{v_{i-3}}^{(0)} + a_{i-1}^{(0)} \psi_{v_{i-1}}^{(0)} + a_{i+1}^{(0)} \psi_{v_{i+1}}^{(0)} + a_{i+3}^{(0)} \psi_{v_{i+3}}^{(0)} \tag{10}$$

where

$$a_i = 1 - \frac{f_i}{2h^2\nu_i^2(8\gamma_i^3)} + \tfrac{3}{8}\frac{f_i^2}{(8h^2\nu_i^2\gamma_i^3)^2}$$

with

$$f_i = \frac{1}{9}\, v_i(v_i-1)(v_i-2)\,a_i^2 + v_i(3v_ia_i+\beta_i)^2 + (v_i+1)[3(v_i+1)a_i+\beta_i]^2 + \frac{1}{9}(v_i+1)(v_i+2)(v_i+3)\,a_i^2;$$

$$a_{i-3} = \frac{-a_i}{3h\nu_i(8\gamma_i^3)^{\frac{1}{2}}}[v_i(v_i-1)(v_i-2)]^{\frac{1}{2}}a_i;$$

$$a_{i-1} = \frac{-a_i}{h\nu_i(8\gamma_i^3)^{\frac{1}{2}}}v_i^{\frac{1}{2}}(3v_ia_i+\beta_i); \tag{11}$$

$$a_{i+1} = \frac{a_i}{h\nu_i(8\gamma_i^3)^{\frac{1}{2}}}(v_i+1)^{\frac{1}{2}}[3(v_i+1)a_i+\beta_i]$$

$$a_{i+3} = \frac{a_i}{3h\nu_i(8\gamma_i^3)^{\frac{1}{2}}}[(v_i+1)(v_i+2)(v_i+3)]^{\frac{1}{2}}a_i$$

and

$$a_i = \frac{-a_{iii}}{6} \quad \text{and} \quad \beta_i = -\gamma_i \sum_{m\neq i}\frac{a_{mmi}(v_m+\frac{1}{2})}{\gamma_m}.$$

The upper suffix in (10) denotes the order of approximation. The zeroth order functions are chosen as the harmonic oscillator eigenfunctions.

To obtain the eigenvalues and eigenfunctions correct to the second order, we substitute the first order eigenfunctions (10) in (7). We now take into account of the quartic terms in the Hamiltonian also. After considerable simplification, the wave function of the ith mode can be written as

$$\left\{-\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial\eta_i^2} + A_{i1}^{(2)}\eta_i + A_{i2}^{(2)}\eta_i^2 + A_{i3}^{(2)}\eta_i^3 + A_{i4}^{(2)}\eta_i^4\right\}\psi_{v_i} = W_i^{(2)}\psi_{v_i} \tag{12}$$

where

$$A_{i1}^{(2)} = \sum_{l}{}' \frac{a_{lli}(v_l + \frac{1}{2})}{2\gamma_l} + \sum_{l}{}' \frac{a_{lli}}{16h^2\nu_l^2\gamma_l^4} Q_l$$

$$+ \sum_{l}{}' \frac{\beta_{llli}}{24\gamma_l^3 h\nu_l} T_l + \sum_{\substack{lm \\ l<m}}{}' \frac{a_{lmi}}{4\gamma_l^2\gamma_m^2 h^2\nu_l\nu_m} R_l R_m$$

$$+ \sum_{lm}{}' \frac{\beta_{llmi}(v_l + \frac{1}{2}) R_m}{4\gamma_m^2\gamma_l h\nu_m};$$

$$A_{i2}^{(2)} = \frac{\lambda_i}{2} + \sum_{l}{}' \frac{a_{lii}R_l}{4\gamma_l^2 h\nu_l} + \sum_{l}{}' \frac{\beta_{llii}}{4\gamma_l}(v_l + \tfrac{1}{2});$$

$$A_{i3}^{(2)} = \frac{a_{iii}}{6} + \frac{1}{12}\sum_{l}{}' \frac{\beta_{liii}}{h\nu_l\gamma_l^2} R_l; \tag{13}$$

$$A_{i4}^{(2)} = \frac{1}{24}\beta_{iiii}$$

and

$$W_i^{(2)} = (v_i + \tfrac{1}{2})h\nu_i + \frac{K_i}{(8\gamma_i^3)h\nu_i} + \frac{a_{iii}}{24\gamma_i^3 h\nu_i} T_i$$

$$+ \frac{\beta_{iiii}}{32\gamma_i^2}\{2(v_i + \tfrac{1}{2})^2 + \tfrac{1}{2}\}$$

$$+ \sum_{l}{}' \frac{\beta_{llii}}{4\gamma_l\gamma_i}(v_l + \tfrac{1}{2})(v_i + \tfrac{1}{2})$$

$$+ \left\{\sum_{m}{}' \frac{a_{iim}}{4\gamma_m^2\gamma_i h\nu_m}(v_i + \tfrac{1}{2}) R_m \right.$$

$$\left. + \sum_{m}{}' \frac{a_{mmi}}{4\gamma_i^2\gamma_m h\nu_i}(v_m + \tfrac{1}{2}) R_i \right\}$$

In the above the accent indicates that the sum excludes the term l or $m = i$.

The quantities R_l, K_l, T_l and Q_l are given by

$$R_l = 3(2v_l + 1)\,a_l + \beta_l;$$

$$K_l = 30a_l^2\left\{(v_l + \tfrac{1}{2})^2 + \frac{7}{60}\right\} + 12a_l\beta_l(v_l + \tfrac{1}{2}) + \beta_l^2;$$

$$T_l = 30a_l\left\{(v_l + \tfrac{1}{2})^2 + \frac{7}{60}\right\} + 6\beta_l(v_l + \tfrac{1}{2}); \tag{15}$$

$$\begin{aligned} Q_l = K_l &+ \tfrac{1}{3}v_l(v_l - 1)(v_l - 2)(3v_la_l + \beta_l)\,a_l \\ &- v_l(v_l + 1)(3v_la_l + \beta_l)(3v_l + 1a_l + \beta_l) \\ &+ \tfrac{1}{3}(v_l + 1)(v_l + 2)(v_l + 3)[3(v_l + 1)\,a_l + \beta_l]\,a_l \end{aligned}$$

$W_i^{(2)}$ gives the expression for the energy of the ith normal mode.

The energy of the whole molecule is

$$\begin{aligned} \epsilon_i^{(2)} = &\sum_l (v_l + \tfrac{1}{2})\,h\nu_l + \sum_l \frac{K_l}{(8\gamma_l^3)\,h\nu_l} + \sum_l \frac{a_{lll}}{24\gamma_l^3 h\nu_l}T_l \\ &+ \sum_l \frac{\beta_{llll}}{32\gamma_l^2}\{2(v_l + \tfrac{1}{2})^2 + \tfrac{1}{2}\} + \sum_{\substack{lm \\ l\neq m}} \frac{a_{llm}R_m}{4\gamma_m^2\gamma_l h\nu_m}(v_l + \tfrac{1}{2}) \\ &+ \sum_{\substack{lm \\ l<m}} \frac{\beta_{llmm}}{4\gamma_l\gamma_m}(v_l + \tfrac{1}{2})(v_m + \tfrac{1}{2}) \end{aligned} \tag{16}$$

Remark

We shall define W^{im} by

$$\begin{aligned} W^{im} = \Big\{ &\frac{a_{iim}}{4\gamma_m^2\gamma_i h\nu_m}(v_i + \tfrac{1}{2})\,R_m + \frac{a_{mmi}(v_m + \tfrac{1}{2})\,R_i}{4\gamma_i^2\gamma_m h\nu_i} \\ &+ \frac{\beta_{mmii}}{4\gamma_m\gamma_i}(v_m + \tfrac{1}{2})(v_i + \tfrac{1}{2})\Big\} \end{aligned} \tag{17}$$

W^{im} denotes the average interaction energy of the ith and mth modes correct to the second order of approximation. The energy of the whole molecule is related to the energy of the individual modes by means of the relation

$$\epsilon_i^{(2)} = \sum_i W_i^{(2)} - \tfrac{1}{2}\sum_i \sum_m W^{im} \tag{18}$$

3. DEGENERACY

We now consider the case of degeneracy of vibrations. For the sake of preciseness, we consider the case in which one of the modes of vibrations of the molecule is doubly degenerate and the remaining modes are all non-degenerate. The more general cases can be discussed on exactly the same lines. Let us denote the modes that are degenerate with one another by the suffixes (N − 1) and N so that $\nu_{N-1} = \nu_N$. Our problem then is to evaluate the energy values and eigenfunctions of the degenerate mode and to find a measure of its splitting due to anharmonicity.

Let us fix our attention on a state in which the different normal modes of the molecule are excited by $v_1, v_2, \ldots\ldots v_{N-2}$ and v_N quantas respectively. The degeneracy of the overtone level of the doubly degenerate mode is then (v_{N+1}). It is well known that the eigenfunctions for the degenerate mode may be written as

$$\psi_m = N_m e^{(-\gamma_N/2)\rho_N^2} F_{v_N}^{l_N}(\sqrt{\gamma_N}\rho_N)\, e^{\pm i l_N \phi_N} \tag{19}$$

where $F_{v_N}^{l_N}(\sqrt{\gamma_N}\rho_N)$ is a polynomial of degree v_N in ρ_N $[= (\eta_{N-1}^2 + \eta_N^2)^{\frac{1}{2}}]$, and l_N is an integer which can assume the values $v_N, v_{N-2}, v_{N-4}\ldots.1$ or 0 depending on whether v_N is odd or even.

Now the symmetry of an overtone level of degree v_N of a mode which falls under a species Γ of the molecule is given by $(\Gamma)^{v_N}$ and this is in general, a linear sum of the irreducible representations of the point group of the molecule. Thus the wave-functions (19) will transform, under a symmetry operation, like a linear sum of the different irreducible representations of the molecule. Or, alternatively, one can form linear combinations of the above $(v_N + 1)$ wave-functions in such a way that the resulting functions fall exclusively each under any one of the irreducible representations of the symmetry group of the molecule.

Let us suppose that the structure of the level under consideration is given by $\sum_\gamma n^{(\gamma)}\Gamma^{(\gamma)}$ where $\Gamma^{(\gamma)}$ stands for the γth species and $n^{(\gamma)}$ is the number of times this species occurs in the reduced representation of the level. It has been shown by Tisza[5] that only wave-functions which either belong to different irreducible representations or to different matrix representations of the same species can have different energy levels and thus the *maximum* number of components into which the level can be split up by the anharmonic terms is $\Sigma n^{(\gamma)}$.

Let us now subject the set of wave-functions (19) to an orthogonal transformation and obtain a new set of functions $\psi_s^{\gamma a}$ $(s = 1, 2, \ldots. v_{N+1})$ such

that each one of these fall exclusively under one of the irreducible representations of the symmetry group of the molecule. In symbols,

$$\psi_S{}^{\gamma a} = \sum_{m=1}^{v_{N+1}} C_{sm}{}^{\gamma a}\psi_m \qquad (s = 1, 2, \ldots . v_{N+1}) \tag{20}$$

where

$$\sum_{m=1}^{(v_{N+1})} (C_{sm}{}^{\gamma a})^2 = 1 \tag{21}$$

and

$$\sum_{m=1}^{v_{N+1}} C_{sm}{}^{\gamma a} C_{s'm}{}^{\gamma' a'} = 0 \qquad (s \neq s')$$

In the above the upper suffix γ denotes the irreducible representation $\Gamma^{(\gamma)}$ under which $\psi_S{}^{\gamma a}$ falls, and a denotes the matrix representation of the irreducible representation. All functions with different γ and a may therefore be expected to have different energies.

The wave function for the ith mode is now given by

$$(H_i - \epsilon_i)\,\psi_{v_i} = 0 \tag{22}$$

where

$$H_i = \int \left(\prod_{k\neq i} \psi^*_{v_k}\right) H \left(\prod_{k\neq i} \psi_{v_k}\right) \prod_{k\neq i} d\eta_k \tag{22 a}$$

In evaluating the above expression, we may notice that the potential energy of the system does not contain the factors η_{N-1} or η_N individually, but involves these only through the sum of their squares (*i.e.*) through

$$(\eta_{N-1}{}^2 + \eta_N{}^2) = \rho_N{}^2.$$

Thus, we have

$$a_{ijN-1} = a_{ijN} = 0$$

$$(i, j = 1, 2, \ldots . N - 2); \quad a_{N-1\,N-1\,N-1} = a_{NNN} = 0;$$

$$\beta_{ijkN-1} = \beta_{ijkN} = \ldots . = \beta_{iNNN} = 0 \ldots .$$

$$(i, j, k = 1, 2, \ldots . N - 2)$$

and

$$a_{iN-1\,N-1} = a_{iNN}; \quad \beta_{ijN-1\,N-1} = \beta_{ijNN}, \text{ etc.}$$

The first-order energy values and eigenfunctions may be obtained by substituting the harmonic oscillator wave functions for the non-degenerate modes and the function $\psi_S{}^{\gamma a}$ for the degenerate one. We get $\epsilon_i{}^{(1)} = \Sigma (v_i + d_i/2)\, h\nu_i$ where the sum is over all modes with distinct frequencies and d_i denotes the degeneracy of the ith mode. The wave equation is given by the same formulæ (8) and (9) with this difference that the constants $A_{i0}{}^{(1)}$ and $A_{i1}{}^{(1)}$ get modified in this by

$$A_{i0}{}^{(1)} = \sum_j{}' \left(v_j + \frac{d_j}{2}\right) h\nu_j$$

and

$$A_{i1}{}^{(1)} = \tfrac{1}{2} \sum_m{}' \frac{a_{mmi}\left(v_m + \frac{d_m}{2}\right)}{\gamma_m} \tag{23}$$

The first order wave equation is therefore still given by (10) with this change that β_i should be defined here by

$$\beta_i = -\gamma_i \Sigma' \frac{a_{mmi}\left(v_m + \frac{d_m}{2}\right)}{\gamma_m} \tag{24}$$

For the degenerate mode, the wave equation is given by

$$\left\{-\frac{h^2}{8\pi^2}\left(\frac{\partial^2}{\partial \eta^2{}_{N-1}} + \frac{\partial^2}{\partial \eta_N{}^2}\right) - W_N{}^{(1)} + \frac{\lambda_N}{2}\rho_N{}^2\right\} \psi_{v_N} = 0 \tag{25}$$

where

$$W_N{}^{(1)} = (v_N + 1)\, h\nu_N.$$

We see that in the first order approximation, anharmonicity does not affect the degenerate mode at all.

The Hamiltonian as well as the eigenvalue for the degenerate mode correct to the second order may be obtained by substituting the wave functions given by (10) and (24) in the variational principle (6). One gets

$$\left\{-\frac{h^2}{8\pi^2}\left(\frac{\partial^2}{\partial \eta^2{}_{N-1}} + \frac{\partial^2}{\partial \eta_N{}^2}\right)\right.$$

$$\left. - W_N{}^{(2)} + A_N{}^{(2)}\rho_N{}^2 + A_N{}^{(4)}\rho_N{}^4\right\} \psi_{v_N} = 0 \tag{26}$$

where

$$A_N^{(4)} = \frac{1}{24}\beta_{NNNN};$$

$$A_N^{(2)} = \frac{\lambda_N}{2} + \sum_{l=1}^{N-2} \frac{a_{NNl}}{4\gamma_l^2 h\nu_l} R_l + \sum_{l=1}^{N-2} \frac{\beta_{NNll}(v_l + \frac{1}{2})}{4\gamma_l};$$

$$W_N^{(2)} = (v_N + 1)\, h\nu_N + \sum_{m=1}^{N-2} \frac{a_{NNm}(v_N + 1)}{4\gamma_m^2 \gamma_N h\nu_m} R_m$$

$$+ \sum_{m} \frac{\beta_{NNmm}}{4\gamma_m \gamma_N}(v_N + 1)(v_m + \tfrac{1}{2})$$

$$+ \frac{\beta_{NNNN}}{16\gamma_N^2}\{(v_N + 1)^2 + \tfrac{1}{3}\} - \frac{\beta_{NNNN}}{48\gamma_N^2}$$

$$\times \{\sum_{m=1}^{v_m+1} (C_{sm}\gamma^a)^2 l_m^2\} \qquad (27)$$

Since the last term in the above may be expected to be different for functions with different γ and a (*i.e.*) for wave functions falling under different irreducible representations or different matrix representations of the same irreducible representation, each level of the degenerate mode will get split into not more than (Σn^γ) sublevels.

The energy of the whole molecule is

$$\epsilon_i^{(2)} = \sum_l \left(v_l + \frac{d_l}{2}\right) h\nu_l + \sum_{l=1}^{N-2} \frac{K_l}{(8\gamma_l^3)\, h\nu_l}$$

$$+ \sum_{l=1}^{N-2} \frac{a_{lll}}{24\gamma_l^3 h\nu_l} T_l + \sum_{\substack{lm \\ m\neq N}} \frac{a_{llm}\left(v_l + \frac{d_l}{2}\right)}{4\gamma_m^2 \gamma_l h\nu_m} R_m$$

$$+ \sum_{l=1}^{N-2} \frac{\beta_{llll}}{16\gamma_l^2}\{(v_l + \tfrac{1}{2})^2 + \tfrac{1}{4}\}$$

$$+ \sum_{\substack{lm \\ l<m}} \frac{\beta_{llmm}}{4\gamma_l \gamma_m}\left(v_l + \frac{d_l}{2}\right)\left(v_m + \frac{d_m}{2}\right)$$

$$+ \frac{\beta_{NNNN}}{16\gamma_N^2}\{(v_N+1)^2+\tfrac{1}{3}\} - \frac{\beta_{NNNN}}{48\gamma_N^2}$$

$$\times \{\sum_{m=1}^{v_{N+1}} (C_{sm}{}^{\gamma a})^2 l_m{}^2\} \tag{28}$$

Nielson has given explicit expressions for the vibrational energy levels of the molecule. His formula for the energy of the molecule may be written as

$$G(v_1, v_2, \ldots.) = \sum_i \left(v_i + \frac{d_i}{2}\right) h\nu_i + \sum_{\substack{i \\ k>i}} \sum^{k} x_{ik} \times \left(v_i + \frac{d_i}{2}\right)\left(v_k + \frac{d_k}{2}\right) + \sum_{i} \sum_{k>i} g_{ik}\, l_i\, l_k \tag{29}$$

In the above, the cross coefficient g_{ik} of the azimuthal quantum numbers l_i and l_k depends on the vibration-rotation interaction of the molecule which is a feature considered in Nielson's work. This explains the absence of the cross terms in the quantum number 'l' in the equation (28). Further, as has been pointed out by Herzberg, the formula (29) gives in general a splitting into fewer levels than what a group theoretical theory would indicate. This is because the wavefunctions used in the evaluation of energy in (29) are the functions (19) and not linear combinations of these falling under different representations of the point group of the molecule. A comparison of (28) with (29) however indicates that the difference is only slight and consists in the replacement of g_{ll} by a coefficient $g_{ll}{}^{\gamma a}$ depending on the symmetry of the state of the sublevel.

For a molecule with several degenerate modes of vibration, the symmetry of a general vibrational level is given by the formula

$$\Gamma = (\Gamma_1)^{v_1} \times (\Gamma_2)^{v_2} \qquad \times (\Gamma^f)^{v_f} \tag{30}$$

where the '$\times$' denotes the direct product multiplication of groups and $v_1, v_2, \ldots. v_f$ are the degrees of excitation of the modes $1, 2, \ldots. f$ respectively. Γ is a linear sum of the different irreducible representations of the molecule, and thus by forming linear sums of products of the wavefunctions of the type (19) which fall exclusively under one of the matrix representation of an irreducible representation of the symmetry group of the molecule, one can evaluate the energy levels of the molecule. If one adopts the standard

perturbation method involving N variables, the expected energy levels may be written in the form

$$G^{\gamma a}(v_1 v_2 \ldots . v_N) = \sum \left(v_i + \frac{d_i}{2}\right) h\nu_i + \sum_i \sum_{k>i} x_{ik}{}^{\gamma a} \times \left(v_i + \frac{d_i}{2}\right)\left(v_k + \frac{d_k}{2}\right) + \sum_i \sum_{k>i} g_{ik}{}^{\gamma a} l_i l_k \qquad (31)$$

In the above, all coefficients $x_{ik}{}^{\gamma a}$ pertaining to non-degenerate modes will be independent of γ and a, but the coefficients $x_{ik}{}^{\gamma a}$ pertaining to degenerate modes and the coefficients $g_{ik}{}^{\gamma a}$ will, in general, be different for levels of different symmetries.

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Summary

The presence of anharmonicity entails the interactions of the normal modes of vibrations, which are independent in the harmonic oscillator approximation. The method of Hartree has been applied to study the mutual interaction of the normal modes, each assumed to be moving in the average potential field of the rest, and to evaluate their wave functions and eigenvalues. It is shown that, to a first order of approximation, normal vibrations belonging to the antisymmetric species do not interact with the rest and suffer no anharmonicity at all. The wave functions and eigenvalues of the different normal modes have been evaluated correct to the second order. The question of degeneracy has been considered and expressions have been given for the energy values of the different sublevels into which an overtone level of a degenerate system may be expected to split up according to group-theoretical considerations.

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