

The Icosahedral Potential and its Applications to the Study of the Anharmonic Effects in the Overtone Levels of the Degenerate Vibrations of Molecules with I_h Symmetry

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The splitting of the overtone levels of the T_{1u} , G_u , and H_g vibrations in molecules with I_h symmetry has been calculated by using the perturbation theory. To do this it was necessary to establish beforehand the icosahedral potential, employing the usual procedure in crystal field theory. The total splitting, predicted by the group theory, is obtained when the anharmonicity up to the sixth power of the coordinates is taken into account. Expressions for the intensities of the infrared-active transitions of T_{1u} vibrations are also proposed.

(Keywords: Anharmonic effects; Degenerate vibrations; Icosahedral potentials)

Das ikosaedrische Potential und seine Anwendung für die Untersuchung der Anharmonizität in den Obertönen der entarteten Schwingungen von Molekülen mit Symmetrie I_h

Die Aufspaltung der Obertöne der Schwingungen T_{1u} , G_u und H_g in Molekülen mit Symmetrie I_h ist unter Verwendung der Störungstheorie berechnet worden. Dafür war es notwendig, das ikosaedrische Potential herzuleiten. Hierbei wurde das übliche Verfahren der Kristallfeld-Theorie angewandt. Die durch die Gruppentheorie vorhergesagte komplette Aufspaltung erhält man, wenn die Anharmonizität bis zur sechsten Potenz in den Koordinaten berücksichtigt wird. Es werden Ausdrücke für die Intensitäten der infrarot-aktiven Übergänge der Schwingungen T_{1u} vorgeschlagen.

Introduction

The harmonic approach has always been extensively used in the study of molecular vibration spectroscopy. Nevertheless, this approach involves

intrinsic limitations, even qualitative ones, which are evident in the case of degenerate molecular vibrations. It is impossible, for example, to describe the multiplet structure of the overtone levels of the degenerate molecular vibrations suggested by the group theory [1].

The predictions of the group theory for such degenerate vibrations coincide with the results of the perturbation theory, where the relevant corrections are made to the different vibrational levels to allow for the anisotropy of the anharmonicity belonging to each particular symmetry [2–5].

In the case of icosahedral molecules the analysis by perturbation theory has not yet been carried out. Furthermore, these molecules are of particular interest because they not only have threefold degenerate vibrations, like cubic molecules [1, 4], but also fourfold and fivefold vibrations [1, 6–8]. The normal vibrations for the chemical species $B_{12}H_{12}^{2-}$ with the icosahedral symmetry are distributed in the following manner, according to the symmetry: $2A_g + T_{1g} + 3T_{1u} + 2T_{2u} + G_g + 4H_g + 2H_u$, among which only T_{1u} is active in infrared and A_g and H_g are active in *Raman*.

In this paper we consider the anharmonic effects in the overtone levels of the T_{1u} and H_g vibrations of icosahedral molecules that are active spectroscopically, and also the G_u vibrations, in order to include all possible cases of degeneracy.

We started from the potential of icosahedral symmetry in order to calculate the necessary corrections to be applied to the vibrational levels. This potential does not appear in the literature and consequently we had to calculate it ourselves. The expressions thus obtained may also be used to calculate the splitting of the crystal field in coordination compounds with icosahedral symmetry.

Theory

The Icosahedral Potential

Following the usual procedure in crystal field theory to obtain the icosahedral potential, we distributed twelve unit charges at the vertices of a regular icosahedron, as shown in Fig. 1. The centre of the icosahedron corresponds to the origin of a system of coordinate axes that, as well as being orthogonal, are equivalent and thus coincide with three twofold rotation axes [9]. This system of axes can be seen in the upper and frontal projection of the icosahedron in Figs. 2(a) and 2(b), respectively. With such a system of axes and bearing in mind the geometrical relationships within an icosahedron [10], the cartesian coordinates of the twelve

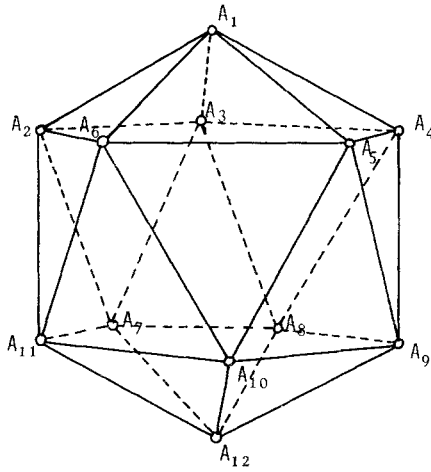


Fig. 1. Spatial arrangement of twelve unit charges at the vertices of a regular icosahedron

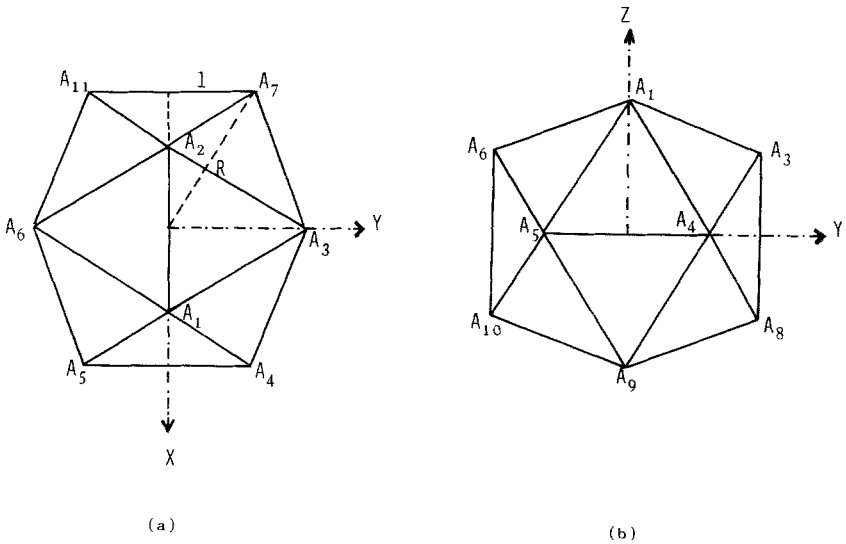


Fig. 2. *a* upper and *b* frontal projections of a regular icosahedron

numbered charges will be, according to *Muetterties* and *Wright* [11], as follows:

$$A_1(1, 0, \varphi); A_2(-1, 0, \varphi); A_3(0, \varphi, 1); A_4(\varphi, 1, 0); A_5(\varphi, -1, 0); A_6(0, -\varphi, 1); A_7(-\varphi, 1, 0); A_8(0, \varphi, -1); A_9(1, 0, -\varphi); A_{10}(0, -\varphi, -1); A_{11}(-\varphi, -1, 0); A_{12}(-1, 0, -\varphi),$$

where “ ϕ ” is the golden number, $1 + (5)^{1/2}/2$, and where the coordinates have been normalized such that the half-length of the edge of the icosahedron is equal to unity.

We then positioned a charge in the interior of the icosahedron at the point P(x, y, z) so that the potential at this point has the general form:

$$V \propto \sum_{i=1}^{i=12} \frac{1}{r_i} \tag{1}$$

where r_i is the distance from the point P(x, y, z) to each of the twelve vertices of the icosahedron. The expressions r_i for each vertex as functions of the cartesian coordinates are the following:

$$\begin{aligned} r_1 &= \{(x - 1)^2 + y^2 + (z - \phi)^2\}^{1/2}; & r_2 &= \{(x + 1)^2 + y^2 + (z - \phi)^2\}^{1/2} \\ r_3 &= \{x^2 + (y - \phi)^2 + (z - 1)^2\}^{1/2}; & r_4 &= \{(x - \phi)^2 + (y - 1)^2 + z^2\}^{1/2} \\ r_5 &= \{(x - \phi)^2 + (y + 1)^2 + z^2\}^{1/2}; & r_6 &= \{x^2 + (y + \phi)^2 + (z - 1)^2\}^{1/2} \\ r_7 &= \{(x + \phi)^2 + (y - 1)^2 + z^2\}^{1/2}; & r_8 &= \{x^2 + (y - \phi)^2 + (z + 1)^2\}^{1/2} \\ r_9 &= \{(x - 1)^2 + y^2 + (z + \phi)^2\}^{1/2}; & r_{10} &= \{x^2 + (y + \phi)^2 + (z + 1)^2\}^{1/2} \\ r_{11} &= \{(x + \phi)^2 + (y + 1)^2 + z^2\}^{1/2}; & r_{12} &= \{(x + 1)^2 + y^2 + (z + \phi)^2\}^{1/2} \end{aligned} \tag{2}$$

These twelve expressions can be grouped into three series, according to their functional form. In this way, series A contains (r_1, r_2, r_9, r_{12}), series B (r_3, r_6, r_8, r_{10}) and series C (r_4, r_5, r_7, r_{11}). The identification of these three series permits us to express (1) in cartesian coordinates with far greater ease, because it is only necessary to carry out the explicit expansion for one of the twelve terms in order to obtain expansions for the other eleven terms of (2). Thus, $1/r_2$ will be:

$$\frac{1}{r_2} = \frac{1}{R} \left\{ \left(\frac{r}{R} \right)^2 + 1 + \frac{2x}{R^2} - \frac{2\phi z}{R^2} \right\}^{-1/2} \tag{3}$$

where $R = (1 + \phi^2)^{1/2}$, as can be seen in Fig. 2 (a) and bearing in mind that $r^2 = x^2 + y^2 + z^2$. Expanding the brackets, which is the power of a polynomial, leads to the result:

$$\begin{aligned} \frac{1}{r_2} &= \frac{1}{R} \sum_{n=0}^{\infty} \sum_{m=0}^n \sum_{s=0}^m \binom{p}{n} \binom{n}{m} \binom{m}{s} (1)^{p-n} \left(\frac{2x}{R^2} \right)^{n-m} \left(-\frac{2\phi z}{R^2} \right)^{m-s} \left(\frac{r^2}{R^2} \right)^s = \\ &= \frac{1}{R} \left\{ 1 + \sum_{n=1}^{\infty} \sum_{m=0}^n \sum_{s=0}^m \binom{-1/2}{n} \binom{n}{m} \binom{m}{s} \left(\frac{2x}{R^2} \right)^{n-m} \left(-\frac{2\phi z}{R^2} \right)^{m-s} \left(\frac{r^2}{R^2} \right)^s \right\} \end{aligned} \tag{4}$$

If we add the terms ($1/r_1, 1/r_2, 1/r_9, 1/r_{12}$) for the four members of series A, those terms that contain odd powers in cartesian coordinates will disappear since they are equal and opposite, and the remaining terms will be repeated as often as there are members in the series. The expansions for series B and C are just the same as that for A, except that in series B z is substituted for x and y for z , and in series C x is substituted for y and y for z .

Once the expansion of the $1/r_1$ expression has been carried out, as described above, and the twelve terms reunited and bearing in mind that $\binom{-k}{h} = (-1)^h \binom{k-h-1}{h}$ the subsequent expression for the icosahedral potential can be written:

$$V(\mathbf{r}) = \frac{12}{R} - \frac{33}{20R^7} \{x^6 + y^6 + z^6 + 3(1 + 7\varphi^{-1})(x^2y^4 + y^2z^4 + z^2x^4) + 3(1 - 7\varphi)(x^4y^2 + y^4z^2 + z^4x^2) + 90x^2y^2z^2\} + \dots \quad (5)$$

The first term of (5) is a simple geometrical constant invariant to K_h and therefore to more symmetry operations than those contained in the I_h group. The second term of (5), however, is only invariant to I_h and, therefore, implies the anisotropy of the icosahedral symmetry in the expression of the potential. To use this potential as an anharmonic correction for the degenerate vibrations of molecules with I_h symmetry we can omit the constant term of (5) and also the constant coefficient that multiplies the brackets of the second term and those which multiply the higher terms; all these latter coefficients will be included in the corresponding constants of anharmonicity, so that, by taking into account only those terms up to and including the sixth power, the expression (5) can now written:

$$V(x, y, z) \propto \{x^6 + y^6 + z^6 + 3(1 + 7\varphi^{-1})(x^2y^4 + y^2z^4 + z^2x^4) + 3(1 - 7\varphi)(x^4y^2 + y^4z^2 + z^4x^2) + 90x^2y^2z^2\} \quad (6)$$

By changing the variables into spherical coordinates and expressing the results as a linear combination of spherical harmonics, the expression (6) will be:

$$V(r, \theta, \varphi) \propto r^6 \left\{ \left(\frac{105}{22}\right)^{1/2} Y_{66}^c - (7)^{1/2} Y_{64}^c - \left(\frac{21}{2}\right)^{1/2} Y_{62}^c + Y_{60}^c \right\} \quad (7)$$

in which we have made use of the normalized spherical harmonics in real form, Y_{lm}^c and Y_{lm}^s , defined by *Bradley and Cracknell* [12].

We have confirmed the expression thus obtained for the icosahedral potential since we were able to identify its sixth power term with one of the basis functions of the trivial representation of I_h , which we obtained as described later on this paper.

Zero Order Eigenfunctions and Selected Perturbations

The eigenfunctions for the stationary states of the isotropic harmonic oscillator in “d” dimensions have the general form given by *Louck* [13]:

$$\Psi_{v,l_{d-1},\dots,l_1}(r, \theta_{d-1}, \dots, \theta_1) = R_{v,l_{d-1}}(r) Y_{l_{d-1},\dots,l_1}(\theta_{d-1}, \dots, \theta_1) \quad (8)$$

with a purely radial part, $R_{v,l_{d-1}}(r)$, and another part which depends only on the generalized spherical harmonics on a hypersphere of $d - 1$ dimensions, $Y_{l_{d-1},\dots,l_1}(\theta_{d-1}, \dots, \theta_1)$, known also as spherical hyperharmonics. Such eigenfunctions, the explicit form of which is given by *Louck* [13], must be invariant to the transformation of the $SU(d)$ group [14].

The parameter “d” can have a maximum value of five, since that is the highest possible degeneracy of the molecular vibrations [1]. Thus, for threefold, fourfold and fivefold degenerate vibrations of molecules with I_h symmetry d equals 3, 4, and 5, respectively.

When $d = 3$ the eigenfunctions (8) are those of the isotropic aharmonic oscillator in three dimensions, invariant to $SU(3)$, and are more widely known as functions of the surface spherical harmonics [15]:

$$\Psi_{v,lm}(r, \theta, \varphi) = R_{v,l}(r) Y_{lm}(\theta, \varphi) \quad (9)$$

where the significance of the vibrational quantum number, v , and of the radial variable, r , remains the same, while $l_2 = 1$ and $l_1 = m$ are now the quantum numbers of the total angular momentum and of the component of this in a arbitrary direction, respectively, and $\theta_2 = \theta$ and $\theta_1 = \varphi$, are now the angular variables of the functions.

In K_h the eigenfunctions have to be bases of its irreducible representations and the use of the eigenfunctions (9) is restricted to the case of the D_{1u} vibrations of the sphere, whereas in its subgroups symmetry-adapted linear combinations of them can be used for T_{1u} vibrations [4]. Therefore, our approach for T_{1u} vibrations of I_h molecules has been to start from the eigenfunctions of the unperturbed levels of the isotropic harmonic oscillator in three dimensions, as a zero-order approach. The angular parts of these eigenfunctions have been replaced by symmetry-adapted linear combinations of these parts. To do this, we have used the operator defined by the expression

$$P_{ij}^k = \frac{n_k}{g} \sum_{\mathbf{R}} D^k(\mathbf{R})_{ij} T_{\mathbf{R}} \quad (10)$$

Table 1. Zero-order eigenfunctions for T_{1u} vibrations of I_h molecules

State	Eigenfunction
$ 0, 0\rangle A_g$	$\psi_{00} = R_{00} Y_{00}$
$ 1, 1\rangle T_{1u}$	$\psi_{11}^{(x)} = R_{11} Y_{11}^c$; $\psi_{11}^{(y)} = R_{11} Y_{11}^s$; $\psi_{11}^{(z)} = R_{11} Y_{10}$
$ 2, 0\rangle A_g$	$\psi_{20} = R_{20} Y_{00}$
$ 2, 2\rangle H_g$	$\psi_{22}^{(a)} = R_{22} Y_{22}^c$; $\psi_{22}^{(b)} = R_{22} Y_{22}^s$; $\psi_{22}^{(c)} = R_{22} Y_{21}^c$; $\psi_{22}^{(d)} = R_{22} Y_{21}^s$; $\psi_{22}^{(e)} = R_{22} Y_{20}$
$ 3, 1\rangle T_{1u}$	$\psi_{31}^{(x)} = R_{31} Y_{11}^c$; $\psi_{31}^{(y)} = R_{31} Y_{11}^s$; $\psi_{31}^{(z)} = R_{31} Y_{10}$
$ 3, 3\rangle T_{2u}$	$\psi_{33}^{(i)} = R_{33} \left(\frac{1}{8}\right)^{\frac{1}{2}} \{ \phi^{-2} Y_{33}^c + \phi(3)^{\frac{1}{2}} Y_{31}^c \}$; $\psi_{33}^{(j)} = R_{33} \left(\frac{1}{8}\right)^{\frac{1}{2}} \{ -\phi^{-2} Y_{33}^s + \phi^{-1}(3)^{\frac{1}{2}} Y_{31}^s \}$ $\psi_{33}^{(k)} = R_{33} \left(\frac{1}{2}\right) \{ (3)^{\frac{1}{2}} Y_{32}^c + Y_{30} \}$
$ 3, 3\rangle G_u$	$\psi_{33}^{(p)} = R_{33} Y_{32}^s$; $\psi_{33}^{(q)} = R_{33} \left(\frac{3}{8}\right)^{\frac{1}{2}} \{ Y_{33}^c - \phi^{-2}(3)^{-\frac{1}{2}} Y_{31}^c \}$ $\psi_{33}^{(r)} = R_{33} \left(\frac{3}{8}\right)^{\frac{1}{2}} \{ -\phi^{-1} Y_{33}^s - \phi^2(3)^{-\frac{1}{2}} Y_{31}^s \}$; $\psi_{33}^{(s)} = R_{33} \left(\frac{3}{4}\right)^{\frac{1}{2}} \{ -(3)^{-\frac{1}{2}} Y_{32}^c + Y_{30} \}$
$ 4, 0\rangle A_g$	$\psi_{40} = R_{40} Y_{00}$
$ 4, 2\rangle H_g$	$\psi_{42}^{(a)} = R_{42} Y_{22}^c$; $\psi_{42}^{(b)} = R_{42} Y_{22}^s$; $\psi_{42}^{(c)} = R_{42} Y_{21}^c$; $\psi_{42}^{(d)} = R_{42} Y_{21}^s$; $\psi_{42}^{(e)} = R_{42} Y_{20}$
$ 4, 4\rangle G_g$	$\psi_{44}^{(p)} = R_{44} \left(\frac{7}{12}\right)^{\frac{1}{2}} \{ \left(\frac{5}{7}\right)^{\frac{1}{2}} Y_{44}^c + Y_{40} \}$; $\psi_{44}^{(q)} = R_{44} \left(\frac{7}{24}\right)^{\frac{1}{2}} \{ (2+\phi^{-2})(7)^{-\frac{1}{2}} Y_{43}^c - \phi Y_{41}^s \}$ $\psi_{44}^{(r)} = R_{44} \left(\frac{7}{24}\right)^{\frac{1}{2}} \{ -(2+\phi^2)(7)^{-\frac{1}{2}} Y_{43}^s + \phi^{-1} Y_{41}^c \}$; $\psi_{44}^{(s)} = R_{44} \left(\frac{1}{12}\right)^{\frac{1}{2}} \{ (5)^{\frac{1}{2}} Y_{44}^s + (7)^{\frac{1}{2}} Y_{42}^s \}$
$ 4, 4\rangle H_g$	$\psi_{44}^{(a)} = R_{44} \left(\frac{1}{12}\right)^{\frac{1}{2}} \{ -(7)^{\frac{1}{2}} Y_{44}^c + (5)^{\frac{1}{2}} Y_{40} \}$; $\psi_{44}^{(b)} = R_{44} Y_{42}^c$ $\psi_{44}^{(c)} = R_{44} \left(\frac{1}{24}\right)^{\frac{1}{2}} \{ -\phi(7)^{\frac{1}{2}} Y_{43}^s - (3-\phi^{-1}) Y_{41}^s \}$; $\psi_{44}^{(d)} = R_{44} \left(\frac{1}{24}\right)^{\frac{1}{2}} \{ \phi^{-1}(7)^{\frac{1}{2}} Y_{43}^c + (3-\phi) Y_{41}^c \}$ $\psi_{44}^{(e)} = R_{44} \left(\frac{5}{12}\right)^{\frac{1}{2}} \{ \left(\frac{7}{5}\right)^{\frac{1}{2}} Y_{44}^s - Y_{42}^s \}$
$ 5, 1\rangle T_{1u}$	$\psi_{51}^{(x)} = R_{51} Y_{11}^c$; $\psi_{51}^{(y)} = R_{51} Y_{11}^s$; $\psi_{51}^{(z)} = R_{51} Y_{10}$
$ 5, 3\rangle T_{2u}$	$\psi_{53}^{(i)} = R_{53} \left(\frac{1}{8}\right)^{\frac{1}{2}} \{ \phi^{-2} Y_{33}^c + \phi(3)^{\frac{1}{2}} Y_{31}^c \}$; $\psi_{53}^{(j)} = R_{53} \left(\frac{1}{8}\right)^{\frac{1}{2}} \{ -\phi^2 Y_{33}^s + \phi^{-1}(3)^{\frac{1}{2}} Y_{31}^s \}$ $\psi_{53}^{(k)} = R_{53} \left(\frac{1}{2}\right) \{ (3)^{\frac{1}{2}} Y_{32}^c + Y_{30} \}$
$ 5, 3\rangle G_u$	$\psi_{53}^{(p)} = R_{53} Y_{32}^s$; $\psi_{53}^{(q)} = R_{53} \left(\frac{3}{8}\right)^{\frac{1}{2}} \{ \phi Y_{33}^c - \phi^{-2}(3)^{-\frac{1}{2}} Y_{31}^c \}$ $\psi_{53}^{(r)} = R_{53} \left(\frac{3}{8}\right)^{\frac{1}{2}} \{ -\phi^{-1} Y_{33}^s - \phi^2(3)^{-\frac{1}{2}} Y_{31}^s \}$; $\psi_{53}^{(s)} = R_{53} \left(\frac{3}{4}\right)^{\frac{1}{2}} \{ -(3)^{-\frac{1}{2}} Y_{32}^c + Y_{30} \}$
$ 5, 5\rangle T_{1u}$	$\psi_{55}^{(x)} = R_{55} \frac{21}{4} (2)^{-\frac{1}{2}} \{ \frac{(3\phi-1)}{6(14)^{\frac{1}{2}}} Y_{55}^c - \frac{\phi^{-1}}{4(14)^{\frac{1}{2}}} Y_{53}^c - \frac{(\phi+3)}{14(3)^{\frac{1}{2}}} Y_{51}^c \}$ $\psi_{55}^{(y)} = R_{55} \frac{21}{4} (2)^{-\frac{1}{2}} \{ \frac{(2-3\phi)}{6(14)^{\frac{1}{2}}} Y_{55}^s + \frac{\phi}{4(14)^{\frac{1}{2}}} Y_{53}^s + \frac{(4-\phi)}{14(3)^{\frac{1}{2}}} Y_{51}^s \}$ $\psi_{55}^{(z)} = R_{55} \frac{21}{4} (2)^{-\frac{1}{2}} \{ \frac{-1}{6} \left(\frac{5}{7}\right)^{\frac{1}{2}} Y_{54}^c - (21)^{-\frac{1}{2}} Y_{52}^c + \frac{1}{14} Y_{50} \}$
$ 5, 5\rangle T_{2u}$	$\psi_{55}^{(i)} = R_{55} \left(\frac{315}{26}\right)^{\frac{1}{2}} \{ 15(1+4\phi) \left(\frac{7}{2}\right)^{\frac{1}{2}} Y_{55}^c - (37-12\phi) \left(\frac{35}{2}\right)^{\frac{1}{2}} Y_{53}^c + (3-4\phi)(735)^{\frac{1}{2}} Y_{51}^c \}$

Table I (continued)

State	Eigenfunction
	$\Psi_{55}^{(j)} = R_{55} \left(\frac{315}{20} \right)^{\frac{1}{2}} \left\{ 15(5-4\phi) \left(\frac{7}{2} \right)^{\frac{1}{2}} Y_{55}^S + (25-12\phi) \left(\frac{35}{2} \right)^{\frac{1}{2}} Y_{53}^S + (4\phi-1)(735) \left(\frac{1}{2} \right)^{\frac{1}{2}} Y_{51}^S \right\}$
	$\Psi_{55}^{(k)} = R_{55} \left(\frac{315}{20} \right)^{\frac{1}{2}} \left\{ -\frac{1}{2}(35) Y_{54}^C - (21) Y_{52}^C + \frac{1}{6} Y_{50}^C \right\}$
$ 5, 5\rangle H_u$	$\Psi_{55}^{(a)} = R_{55} Y_{52}^{-S}; \quad \Psi_{55}^{(b)} = R_{55} Y_{54}^{-S}; \quad \Psi_{55}^{(c)} = R_{55} \frac{1}{8} \left(\frac{105}{2} \right)^{\frac{1}{2}} \left\{ \frac{(3-\phi)}{(14)^{\frac{1}{2}}} Y_{55}^C - \frac{(5+\phi)}{(70)^{\frac{1}{2}}} Y_{53}^C + \frac{\phi^2}{(15)^{\frac{1}{2}}} Y_{51}^C \right\}$
	$\Psi_{55}^{(d)} = R_{55} \frac{1}{32} \left(\frac{105}{2} \right)^{\frac{1}{2}} \left\{ \frac{(9+4\phi)}{(14)^{\frac{1}{2}}} Y_{55}^S + \frac{(15-4\phi)}{(70)^{\frac{1}{2}}} Y_{53}^S + \frac{(11-4\phi)}{(15)^{\frac{1}{2}}} Y_{51}^S \right\}$
	$\Psi_{55}^{(e)} = R_{55} \frac{1}{8} \left(\frac{105}{2} \right)^{\frac{1}{2}} \left\{ (35)^{-\frac{1}{2}} Y_{54}^C + 2(21)^{-\frac{1}{2}} Y_{52}^C + Y_{50}^C \right\}$
$ 6, 0\rangle A_g$	$\Psi_{60} = R_{60} Y_{00}$
$ 6, 2\rangle H_g$	$\Psi_{62}^{(a)} = R_{62} Y_{22}^C; \quad \Psi_{62}^{(b)} = R_{62} Y_{22}^S; \quad \Psi_{62}^{(c)} = R_{62} Y_{21}^C; \quad \Psi_{62}^{(d)} = R_{62} Y_{21}^S; \quad \Psi_{62}^{(e)} = R_{62} Y_{20}$
$ 6, 4\rangle G_g$	$\Psi_{64}^{(p)} = R_{64} \left(\frac{7}{12} \right)^{\frac{1}{2}} \left\{ \left(\frac{7}{5} \right)^{\frac{1}{2}} Y_{44}^C + Y_{40} \right\}; \quad \Psi_{64}^{(q)} = R_{64} \left(\frac{7}{24} \right)^{\frac{1}{2}} \left\{ (2+\phi-2)(7)^{-\frac{1}{2}} Y_{43}^S - \phi Y_{41}^S \right\}$
	$\Psi_{64}^{(r)} = R_{64} \left(\frac{7}{24} \right)^{\frac{1}{2}} \left\{ -(2+\phi^2)(7)^{-\frac{1}{2}} Y_{43}^C + \phi^{-1} Y_{41}^C \right\}; \quad \Psi_{64}^{(s)} = R_{64} \left(\frac{1}{12} \right)^{\frac{1}{2}} \left\{ (5)^{\frac{1}{2}} Y_{44}^S + (7)^{\frac{1}{2}} Y_{42}^S \right\}$
$ 6, 4\rangle H_g$	$\Psi_{64}^{(a)} = R_{64} \left(\frac{1}{12} \right)^{\frac{1}{2}} \left\{ -(7)^{\frac{1}{2}} Y_{44}^C + (5)^{\frac{1}{2}} Y_{40} \right\}; \quad \Psi_{64}^{(b)} = R_{64} Y_{42}^{-C}$
	$\Psi_{64}^{(c)} = R_{64} \left(\frac{1}{24} \right)^{\frac{1}{2}} \left\{ -\phi(7)^{\frac{1}{2}} Y_{43}^S - (3-\phi^{-1}) Y_{41}^S \right\}; \quad \Psi_{64}^{(d)} = R_{64} \left(\frac{1}{24} \right)^{\frac{1}{2}} \left\{ \phi^{-1}(7)^{\frac{1}{2}} Y_{43}^C + (3-\phi) Y_{41}^C \right\}$
	$\Psi_{64}^{(e)} = R_{64} \left(\frac{5}{12} \right)^{\frac{1}{2}} \left\{ \left(\frac{7}{5} \right)^{\frac{1}{2}} Y_{44}^S - Y_{42}^S \right\}$
$ 6, 6\rangle A_g$	$\Psi_{66} = R_{66} \frac{(11)}{16} \left\{ \left(\frac{105}{22} \right)^{\frac{1}{2}} Y_{66}^C - (7)^{\frac{1}{2}} Y_{64}^C - \left(\frac{21}{2} \right)^{\frac{1}{2}} Y_{62}^C + Y_{60} \right\}$
$ 6, 6\rangle T_{1g}$	$\Psi_{66}^{(x)} = R_{66} \frac{1}{8\phi} \left(\frac{33}{2} \right)^{\frac{1}{2}} \left\{ \frac{(4\phi-3)}{(66)^{\frac{1}{2}}} Y_{65}^S + \frac{(4\phi+3)}{(10)^{\frac{1}{2}}} Y_{63}^S + Y_{61}^S \right\}$
	$\Psi_{66}^{(y)} = R_{66} \frac{1}{8\phi} \left(\frac{33}{2} \right)^{\frac{1}{2}} \left\{ \frac{(7\phi+3)}{(66)^{\frac{1}{2}}} Y_{65}^{-C} + \frac{(\phi-3)}{(10)^{\frac{1}{2}}} Y_{63}^{-C} + \phi^2 Y_{61}^{-C} \right\}$
	$\Psi_{66}^{(z)} = R_{66} \frac{3}{8\phi} \left(\frac{11}{2} \right)^{\frac{1}{2}} \left\{ \frac{(\phi+2)}{(22)^{\frac{1}{2}}} Y_{66}^S - \frac{2\phi}{3} Y_{64}^S - \frac{(\phi+2)}{(30)^{\frac{1}{2}}} Y_{62}^S \right\}$
$ 6, 6\rangle H_g$	$\Psi_{66}^{(a)} = R_{66} \left(\frac{1}{4} \right) \left\{ (2)^{\frac{1}{2}} Y_{64}^C + (14)^{\frac{1}{2}} Y_{60} \right\}; \quad \Psi_{66}^{(b)} = R_{66} \left(\frac{1}{4} \right) \left\{ (11)^{\frac{1}{2}} Y_{66}^C + (5)^{\frac{1}{2}} Y_{62}^C \right\}$
	$\Psi_{66}^{(c)} = R_{66} \frac{1}{8} (26-6\phi)^{-\frac{1}{2}} \left\{ (4\phi-1) \left(\frac{3}{22} \right)^{\frac{1}{2}} Y_{65}^S + (19-12\phi) \left(\frac{5}{242} \right)^{\frac{1}{2}} Y_{63}^S - Y_{61}^S \right\}$
	$\Psi_{66}^{(d)} = R_{66} \frac{1}{8} (26-6\phi)^{-\frac{1}{2}} \left\{ (5\phi-7) \left(\frac{3}{22} \right)^{\frac{1}{2}} Y_{65}^C + (5+9\phi) \left(\frac{5}{242} \right)^{\frac{1}{2}} Y_{63}^C + \frac{(13-3\phi)}{11} Y_{61}^C \right\}$
	$\Psi_{66}^{(e)} = R_{66} \frac{1}{16} (26-6\phi)^{-\frac{1}{2}} \left\{ (2-3\phi) (22)^{\frac{1}{2}} Y_{66}^S + 4(\phi-8) (3)^{\frac{1}{2}} Y_{64}^S + 5(3\phi-2) (10)^{\frac{1}{2}} Y_{62}^S \right\}$
$ 6, 6\rangle G_g$	$\Psi_{66}^{(p)} = R_{66} \frac{(21)}{32} \left\{ \left(\frac{110}{21} \right)^{\frac{1}{2}} Y_{66}^{-C} - 2(7)^{\frac{1}{2}} Y_{64}^C + 11 \left(\frac{21}{21} \right)^{\frac{1}{2}} Y_{62}^C + 2Y_{60} \right\}$
	$\Psi_{66}^{(q)} = R_{66} \frac{(41-15\phi)^{-\frac{1}{2}}}{8} \left\{ (9-4\phi) \left(\frac{33}{2} \right)^{\frac{1}{2}} Y_{65}^S + \frac{(23-3\phi\phi)}{(10)^{\frac{1}{2}}} Y_{63}^S + 29Y_{61}^S \right\}$
	$\Psi_{66}^{(r)} = R_{66} \frac{(41-15\phi)^{-\frac{1}{2}}}{8} \left\{ (\phi-5) \left(\frac{33}{2} \right)^{\frac{1}{2}} Y_{65}^C + \frac{(37-3\phi\phi)}{(10)^{\frac{1}{2}}} Y_{63}^C + (41-15\phi) Y_{61}^C \right\}$

Table 1 (continued)

State	Eigenfunction
	$\psi_{66}^{(s)} = R_{66} \frac{(41-15\phi)^{-\frac{1}{2}}}{16} \{ (14-3\phi)(22)^{\frac{1}{2}} Y_{66}^s + (5\phi-4)(48)^{\frac{1}{2}} Y_{64}^s + (14-3\phi) \left(\frac{98}{5}\right)^{\frac{1}{2}} Y_{62}^s \}$
17, 1 > T _{1u}	$\psi_{71}^{(x)} = R_{71} Y_{11}^c; \quad \psi_{71}^{(y)} = R_{71} Y_{11}^s; \quad \psi_{71}^{(z)} = R_{71} Y_{10}$
17, 3 > G _u	$\psi_{73}^{(p)} = R_{73} Y_{32}^s; \quad \psi_{73}^{(q)} = R_{73} \left(\frac{3}{8}\right)^{\frac{1}{2}} \{ \phi Y_{33}^c - \phi^{-2}(3)^{-\frac{1}{2}} Y_{31}^c \};$
	$\psi_{73}^{(r)} = R_{73} \left(\frac{3}{8}\right)^{\frac{1}{2}} \{ -\phi^{-1} Y_{33}^s - \phi^2(3)^{-\frac{1}{2}} Y_{31}^s \}; \quad \psi_{73}^{(s)} = R_{73} \left(\frac{3}{4}\right)^{\frac{1}{2}} \{ -(3)^{-\frac{1}{2}} Y_{32}^c + Y_{30} \}$
17, 3 > T _{2u}	$\psi_{73}^{(i)} = R_{73} \left(\frac{1}{8}\right)^{\frac{1}{2}} \{ \phi^{-2} Y_{33}^c + \phi(3)^{\frac{1}{2}} Y_{31}^c \}; \quad \psi_{73}^{(j)} = R_{73} \left(\frac{1}{8}\right)^{\frac{1}{2}} \{ \phi^{-2} Y_{33}^s + \phi^{-1}(3)^{\frac{1}{2}} Y_{31}^s \}$
	$\psi_{73}^{(k)} = R_{73} \left(\frac{1}{2}\right) \{ (3)^{\frac{1}{2}} Y_{32}^c + Y_{30} \}$
17, 5 > T _{1u}	$\psi_{75}^{(x)} = R_{75} \frac{21}{4} (2)^{-\frac{1}{2}} \left\{ \frac{(3\phi-1)}{6(14)^{\frac{1}{2}}} Y_{55}^c - \frac{\phi^{-1}}{4(14)^{\frac{1}{2}}} Y_{53}^c - \frac{(\phi+3)}{14(3)^{\frac{1}{2}}} Y_{51}^c \right\}$
	$\psi_{75}^{(y)} = R_{75} \frac{21}{4} (2)^{-\frac{1}{2}} \left\{ \frac{(2-3\phi)}{6(14)^{\frac{1}{2}}} Y_{55}^s + \frac{\phi}{4(14)^{\frac{1}{2}}} Y_{53}^s + \frac{(4-\phi)}{14(3)^{\frac{1}{2}}} Y_{51}^s \right\}$
	$\psi_{75}^{(z)} = R_{75} \frac{21}{4} (2)^{-\frac{1}{2}} \left\{ -\frac{1}{6} \left(\frac{5}{7}\right)^{\frac{1}{2}} Y_{54}^c - (21)^{-\frac{1}{2}} Y_{52}^c + \frac{1}{14} Y_{50} \right\}$
17, 5 > T _{2u}	$\psi_{75}^{(i)} = R_{75} \left(\frac{315}{20}\right)^{\frac{1}{2}} \{ 15(1+4\phi) \left(\frac{7}{2}\right)^{\frac{1}{2}} Y_{55}^c - (37-12\phi) \left(\frac{35}{2}\right)^{\frac{1}{2}} Y_{53}^c + (3-4\phi)(735)^{\frac{1}{2}} Y_{51}^c \}$
	$\psi_{75}^{(j)} = R_{75} \left(\frac{315}{20}\right)^{\frac{1}{2}} \{ 15(5-4\phi) \left(\frac{7}{2}\right)^{\frac{1}{2}} Y_{55}^s + (25-12\phi) \left(\frac{35}{2}\right)^{\frac{1}{2}} Y_{53}^s + (4\phi-1)(735)^{\frac{1}{2}} Y_{51}^s \}$
	$\psi_{75}^{(k)} = R_{75} \left(\frac{315}{20}\right)^{\frac{1}{2}} \left\{ -\frac{1}{2}(35)^{-\frac{1}{2}} Y_{54}^c - (21)^{-\frac{1}{2}} Y_{52}^c + \frac{1}{6} Y_{50} \right\}$
17, 5 > H _u	$\psi_{75}^{(a)} = R_{75} Y_{55}^{-s}; \quad \psi_{75}^{(b)} = R_{75} Y_{55}^s; \quad \psi_{75}^{(c)} = R_{75} \frac{1}{8} \left(\frac{105}{2}\right)^{\frac{1}{2}} \left\{ \frac{(3-\phi)}{(14)^{\frac{1}{2}}} Y_{55}^c - \frac{(5+\phi)}{(70)^{\frac{1}{2}}} Y_{53}^c + \frac{\phi^2}{(15)^{\frac{1}{2}}} Y_{51}^c \right\}$
	$\psi_{75}^{(d)} = R_{75} \frac{1}{32} \left(\frac{105}{2}\right)^{\frac{1}{2}} \left\{ \frac{(9+4\phi)}{(14)^{\frac{1}{2}}} Y_{55}^s + \frac{(15-4\phi)}{(70)^{\frac{1}{2}}} Y_{53}^s + \frac{(11-4\phi)}{(15)^{\frac{1}{2}}} Y_{51}^s \right\}$
	$\psi_{75}^{(e)} = R_{75} \frac{1}{8} \left(\frac{105}{2}\right)^{\frac{1}{2}} \left\{ (35)^{-\frac{1}{2}} Y_{54}^c + 2(21)^{-\frac{1}{2}} Y_{52}^c + Y_{50} \right\}$
17, 7 > T _{1u}	$\psi_{77}^{(x)} = R_{77} \frac{1}{32} \left(\frac{11}{5}\right)^{\frac{1}{2}} \left\{ \frac{(1365)}{11} Y_{77}^c - (21+2\phi) \left(\frac{3}{11}\right)^{\frac{1}{2}} Y_{75}^c + (5-6\phi)(3)^{\frac{1}{2}} Y_{73}^c + (1+6\phi) Y_{71}^c \right\}$
	$\psi_{77}^{(y)} = R_{77} \frac{1}{32} \left(\frac{11}{5}\right)^{\frac{1}{2}} \left\{ \frac{(1365)}{11} Y_{77}^s + (2\phi-23) \left(\frac{3}{11}\right)^{\frac{1}{2}} Y_{75}^s + (1-6\phi)(3)^{\frac{1}{2}} Y_{73}^s - (6\phi-7) Y_{71}^s \right\}$
	$\psi_{77}^{(z)} = R_{77} \frac{1}{32} \left(\frac{11}{5}\right)^{\frac{1}{2}} \left\{ \left(\frac{390}{11}\right)^{\frac{1}{2}} Y_{76}^c - 2(33)^{\frac{1}{2}} Y_{74}^c - (270)^{\frac{1}{2}} Y_{72}^c + 2(7)^{\frac{1}{2}} Y_{70} \right\}$
17, 7 > T _{2u}	$\psi_{77}^{(i)} = R_{77} \frac{1}{64} \left(\frac{3}{35}\right)^{\frac{1}{2}} \left\{ 5 \left(\frac{1001}{3}\right)^{\frac{1}{2}} Y_{77}^c + 7 \left(\frac{11}{3}\right)^{\frac{1}{2}} (4\phi-9) Y_{75}^c + 7(3)^{-\frac{1}{2}} (3+28\phi) Y_{73}^c + 7(8\phi-11) Y_{71}^c \right\}$
	$\psi_{77}^{(j)} = R_{77} \frac{1}{64} \left(\frac{3}{35}\right)^{\frac{1}{2}} \left\{ 5 \left(\frac{1001}{3}\right)^{\frac{1}{2}} Y_{77}^{-s} - 7 \left(\frac{11}{3}\right)^{\frac{1}{2}} (5+4\phi) Y_{75}^s + 7(3)^{-\frac{1}{2}} (28\phi-31) Y_{73}^s - 7(3+8\phi) Y_{71}^s \right\}$
	$\psi_{77}^{(k)} = R_{77} \frac{1}{64} \left(\frac{3}{35}\right)^{\frac{1}{2}} \left\{ 7 \left(\frac{1430}{3}\right)^{\frac{1}{2}} Y_{76}^c - 14 \left(\frac{11}{3}\right)^{\frac{1}{2}} Y_{74}^c + 7 \left(\frac{10}{3}\right)^{\frac{1}{2}} Y_{72}^c + 58(7)^{\frac{1}{2}} Y_{70} \right\}$
17, 7 > G _u	$\psi_{77}^{(p)} = R_{77} \frac{(6)^{-\frac{1}{2}}}{2} \{ (11)^{\frac{1}{2}} Y_{76}^s + (13)^{\frac{1}{2}} Y_{72}^s \}$
	$\psi_{77}^{(q)} = R_{77} \frac{1}{32} \left(\frac{13}{5}\right)^{\frac{1}{2}} \left\{ \frac{(1155)}{13} Y_{77}^c - (5+2\phi) \left(\frac{11}{3}\right)^{\frac{1}{2}} Y_{75}^c + \frac{(7\phi+2)}{(3)^{\frac{1}{2}}} Y_{73}^c + (9-10\phi) Y_{71}^c \right\}$
	$\psi_{77}^{(r)} = R_{77} \frac{1}{32} \left(\frac{13}{5}\right)^{\frac{1}{2}} \left\{ \frac{(1155)}{13} Y_{77}^s - (7-2\phi) \left(\frac{11}{3}\right)^{\frac{1}{2}} Y_{75}^s - \frac{(5+2\phi)}{(3)^{\frac{1}{2}}} Y_{73}^s + (10\phi-1) Y_{71}^s \right\}$
	$\psi_{77}^{(s)} = R_{77} \frac{1}{16} \left(\frac{13}{5}\right)^{\frac{1}{2}} \left\{ 5 \left(\frac{55}{8}\right)^{\frac{1}{2}} Y_{76}^c - (33)^{\frac{1}{2}} Y_{74}^c + 7 \left(\frac{5}{6}\right)^{\frac{1}{2}} Y_{72}^c + (7)^{\frac{1}{2}} Y_{70} \right\}$

Table 1 (continued)

State	Eigenfunction
$17, 7 > H_u$	$\psi_{77}^{(a)} = R_{77} Y_{74}^S; \quad \psi_{77}^{(b)} = R_{77} \frac{(6)^{-\frac{1}{2}}}{2} \{ (13)^{\frac{1}{2}} Y_{76}^{-S} + (11)^{\frac{1}{2}} Y_{72}^S \}$ $\psi_{77}^{(c)} = R_{77} \frac{1}{64} \left(\frac{11}{5}\right)^{\frac{1}{2}} \{ 195 \left(\frac{7}{429}\right)^{\frac{1}{2}} Y_{77}^C + \frac{(67-44\theta)}{(33)^{\frac{1}{2}}} Y_{75}^C + \frac{(29-28\theta)}{(3)^{\frac{1}{2}}} Y_{73}^C - (21+8\theta) Y_{71}^C \}$ $\psi_{77}^{(d)} = R_{77} \frac{1}{64} \left(\frac{11}{5}\right)^{\frac{1}{2}} \{ 195 \left(\frac{7}{429}\right)^{\frac{1}{2}} Y_{77}^{-S} + \frac{(23+44\theta)}{(33)^{\frac{1}{2}}} Y_{75}^S - \frac{(1+28\theta)}{(3)^{\frac{1}{2}}} Y_{73}^S - (29-8\theta) Y_{71}^S \}$ $\psi_{77}^{(e)} = R_{77} \frac{1}{64} \left(\frac{11}{5}\right)^{\frac{1}{2}} \{ \left(\frac{143\theta}{3}\right)^{\frac{1}{2}} Y_{76}^C + \frac{5\theta}{11} (33)^{\frac{1}{2}} Y_{74}^C - \left(\frac{10}{3}\right)^{\frac{1}{2}} Y_{72}^C + 10(7)^{\frac{1}{2}} Y_{70}^C \}$

where $D^k(R)_{ij}$ are the elements of the matrices of the representation Γ_k . In order to make use of this expression the explicit matrix representation of the I_h group [16] must be available beforehand. The eigenfunctions obtained in this way are shown in Table 1. They have been tabulated as far as $v = 7$ as they come in use later in the calculation of the perturbed eigenfunctions and the intensities of the active transitions in infrared for such T_{1u} vibrations. The states have been denoted as $|v, l > \Gamma$, where “v” and “l” have the same significance as above, and Γ represent the species of symmetry of the state associated with “v” and “l”.

We have identified the eigenfunctions up to $v = 4$ with those irreducible icosahedral tensors of fourth rank that are not zero when their expressions are transformed to spherical coordinates [9].

For G_u and H_g vibrations we could have followed a process similar to the one described for T_{1u} , with the aim of obtaining eigenfunctions that could be used as a zero order approach in the calculus of the perturbations. In other words, we could have taken as radial parts of the eigenfunctions those of the fourfold and fivefold isotropic harmonic oscillator, and as angular parts symmetrized linear combinations of the spherical hyperharmonics in three and four dimensions. Nevertheless, assuming that the icosahedral potential (7), which will act as a perturbation on all the vibrations of icosahedral molecules, is defined in only one euclidian three-dimensional space, we decided to use the radial parts of the eigenfunctions of fourfold and fivefold isotropic harmonic oscillator as the radial parts of the eigenfunctions for the G_u and H_g vibrations, since these are the only known radial parts and symmetrized linear combination of surface spherical harmonics as angular parts. Such linear combinations imply the molecular anisotropy in the eigenfunctions. This process has been used before in the study of degenerate vibrations of molecules belonging to other point symmetry groups [3–5] and can be justified on the basis of *Wigner* and *Eckart's* theorem [17–18], which states that the matrix elements obtained with such eigenfunctions must be

proportional to the ones obtained starting from the true eigenfunctions. It is thus possible to include the different proportionality constants in the corresponding anharmonicity constants.

According to the group theory [1], the successive overtone levels of any particular vibration must split into as many states as there are irreducible representations resulting from the reduction of the v^{th} symmetrical power of the irreducible representation of the first excited state. We obtained the angular parts of the zero order eigenfunctions for the G_u and H_g vibrations of I_h molecules by methodically constructing the bases for the irreducible representations which result from the reduction of $[G_u^v]$ and $[H_g^v]$, respectively. These bases have been symmetrized using the operator defined by (10), starting from the basis $\{Y_{32}^s, (3/8)^{1/2} [\varphi Y_{33}^c - \varphi^{-2} (3)^{-1/2} Y_{31}^c], (3/8)^{1/2} [-\varphi^{-1} Y_{33}^s - \varphi^2 (3)^{-1/2} Y_{31}^s], (3/4)^{1/2} [-(3)^{-1/2} Y_{32}^c + Y_{30}]\}$ of G_u and $\{Y_{20}, Y_{21}^{c,s}, Y_{22}^{c,s}\}$ of H_g .

The zero order eigenfunctions completed for the G_u and H_g vibrations appear in Tables 2 and 3, respectively. For H_g the notation $|v, l > \Gamma$ has been retained and although the parameter "l" does not have the same significance as in T_{1u} , it nevertheless allow us to unambiguously relate each state of such H_g vibrations to that of the D_{2g} vibrations of the sphere, from which they come through descent in symmetry. It also allows us to identify perfectly the eigenfunctions that must be associated with them. In this case of the G_u vibrations only the notation $|v > \Gamma$ has been used since their parentage with the D_{3u} vibrations of the sphere is of fractional type and, consequently, different mixed values of "l" will appear in the same eigenfunction.

The anharmonicity that will act as a perturbation of the harmonic model for all the vibrations of I_h molecules will be as follows:

$$\Delta H = \beta r^4 + \gamma r^6 + \gamma' r^6 \left\{ \left(\frac{105}{22} \right)^{1/2} Y_{66}^c - (7)^{1/2} Y_{64}^c - \left(\frac{21}{2} \right)^{1/2} Y_{62}^c + Y_{60} \right\} \quad (11)$$

where the third term of equation (11) is the sixth order icosahedral potential, obtained in the above section and the first and second terms have been included because, if they are invariant to K_h , they will also be invariant to its I_h subgroup.

Results and Discussion

According to *Tisza* [1], the successive overtone levels of the T_{1u} , G_u and H_g vibrations of I_h molecules must split as follows:

v	T _{1u}	G _u	H _g
0	A _g	A _g	A _g
1	T _{1u}	G _u	H _g
2	[T _{1u} ²] = A _g + H _g	[G _u ²] = A _g + G _g + H _g	[H _g ²] = A _g + G _g + 2 H _g
3	[T _{1u} ³] = T _{1u} + T _{2u} + G _u	[G _u ³] + A _u + T _{1u} + T _{2u} + 2 G _u + H _u	[H _g ³] = 2 A _g + T _{1g} + T _{2g} + 3 G _g + 3 H _g

Table 2. Zero-order eigenfunctions for G_u vibrations of I_h molecules

State	Eigenfunctions
0> A _g	$\psi_{00} = R_{00} Y_{00}$
1> G _u	$\psi_{11}^{(p)} = R_{11} Y_{32}^s; \psi_{11}^{(q)} = R_{11} (\frac{3}{8})^{\frac{1}{2}} (\phi Y_{33}^c - \phi^{-2} (3)^{-\frac{1}{2}} Y_{31}^c);$
	$\psi_{11}^{(r)} = R_{11} (\frac{3}{8})^{\frac{1}{2}} \{-\phi^{-1} Y_{33}^s - \phi^2 (3)^{-\frac{1}{2}} Y_{31}^s\}; \psi_{11}^{(s)} = R_{11} (\frac{3}{4})^{\frac{1}{2}} \{- (3)^{-\frac{1}{2}} Y_{32}^c + Y_{30}^s\}$
2> A _g	$\psi_{20} = R_{20} \frac{1}{64} (\frac{3003}{2})^{\frac{1}{2}} \{ 5 (\frac{10}{3003})^{\frac{1}{2}} Y_{66}^c - \frac{10}{3} (91)^{-\frac{1}{2}} Y_{64}^c - 5 (\frac{2}{273})^{\frac{1}{2}} Y_{62}^c + \frac{10}{21} (13)^{-\frac{1}{2}} Y_{60}^c + \frac{32}{21} Y_{00}^s \}$
2> G _g	$\psi_{22}^{(p)} = R_{22} (\frac{429}{4})^{\frac{1}{2}} \{ -\frac{5}{8} (13)^{-\frac{1}{2}} [(\frac{5}{462})^{\frac{1}{2}} Y_{66}^c - \frac{1}{11} (7)^{\frac{1}{2}} Y_{64}^c + (42)^{-\frac{1}{2}} Y_{62}^c + \frac{1}{11} Y_{60}^c] + \frac{2}{33} [(\frac{5}{7})^{\frac{1}{2}} Y_{44}^c + Y_{40}^s] \}$
	$\psi_{22}^{(q)} = R_{22} (\frac{429}{4})^{\frac{1}{2}} \{ -\frac{5}{2} (11193-4095\phi)^{-\frac{1}{2}} [(9-4\phi) (\frac{3}{88})^{\frac{1}{2}} Y_{65}^s + \frac{(23-36\phi)}{22} (10)^{-\frac{1}{2}} Y_{63}^s + \frac{29}{22} Y_{61}^s] +$ $+ \frac{(2)}{33} [(4-\phi) (7)^{-\frac{1}{2}} Y_{43}^s - \phi Y_{41}^s] \}$
	$\psi_{22}^{(r)} = R_{22} (\frac{429}{4})^{\frac{1}{2}} \{ -\frac{5}{2} (11193-4095\phi)^{-\frac{1}{2}} [(\phi+5) (\frac{3}{88})^{\frac{1}{2}} Y_{65}^c + \frac{(37-39\phi)}{22} (10)^{-\frac{1}{2}} Y_{63}^c + \frac{(41-15\phi)}{22} Y_{61}^c] +$ $+ -\frac{(2)}{33} [(3+\phi) (7)^{-\frac{1}{2}} Y_{43}^c + \phi^{-1} Y_{41}^c] \}$
2> H _g	$\psi_{22}^{(a)} = R_{22} \frac{3}{16} (455)^{\frac{1}{2}} \{ \frac{(-5)}{11} (\frac{2}{91})^{\frac{1}{2}} [\frac{1}{2} (\frac{55}{3})^{\frac{1}{2}} Y_{66}^c + \frac{(2)}{3} Y_{64}^c + \frac{5}{2} (3)^{-\frac{1}{2}} Y_{62}^c + \frac{1}{3} (\frac{7}{2})^{\frac{1}{2}} Y_{60}^c] +$ $+ \frac{1}{33} [\frac{1}{2} (\frac{5}{7})^{\frac{1}{2}} Y_{44}^c - Y_{42}^c + \frac{5}{14} Y_{40}^c] - \frac{8}{21} (5)^{-\frac{1}{2}} Y_{20}^s \}$
	$\psi_{22}^{(b)} = R_{22} \frac{1}{16} (1365)^{\frac{1}{2}} \{ -\frac{10}{11} (\frac{2}{91})^{\frac{1}{2}} [\frac{1}{4} (\frac{11}{3})^{\frac{1}{2}} Y_{66}^c + \frac{1}{2} (\frac{5}{2})^{\frac{1}{2}} Y_{64}^c + \frac{1}{4} (\frac{5}{3})^{\frac{1}{2}} Y_{62}^c + \frac{1}{2} (\frac{35}{2})^{\frac{1}{2}} Y_{60}^c] +$ $+ \frac{1}{11} [\frac{1}{6} (7)^{\frac{1}{2}} Y_{44}^c - \frac{1}{7} (5)^{\frac{1}{2}} Y_{42}^c - \frac{1}{6} (5)^{\frac{1}{2}} Y_{40}^c] - \frac{8}{7} (15)^{-\frac{1}{2}} Y_{22}^s \}$
	$\psi_{22}^{(c)} = R_{22} \frac{1}{8} (455)^{\frac{1}{2}} \{ 5 (1183-273\phi)^{-\frac{1}{2}} [\frac{1}{4} (2-3\phi) (\frac{2}{11})^{\frac{1}{2}} Y_{66}^s + \frac{1}{11} (3)^{\frac{1}{2}} (\phi-8) Y_{64}^s + \frac{5}{22} (\frac{5}{2})^{\frac{1}{2}} (3\phi-2) Y_{62}^s] -$ $- \frac{2}{77} (\frac{5}{3})^{\frac{1}{2}} [(\frac{7}{5})^{\frac{1}{2}} Y_{44}^s - Y_{42}^s] - \frac{4}{7} (5)^{-\frac{1}{2}} Y_{22}^s \}$
	$\psi_{22}^{(d)} = R_{22} \frac{1}{8} (455)^{\frac{1}{2}} \{ 5 (1183-273\phi)^{-\frac{1}{2}} [\frac{1}{2} (5\phi-7) (\frac{3}{22})^{\frac{1}{2}} Y_{65}^c + \frac{1}{22} (\frac{5}{2})^{\frac{1}{2}} (5+9\phi) Y_{63}^c + \frac{1}{22} (13-3\phi) Y_{61}^c] -$ $- \frac{2}{77} (6)^{-\frac{1}{2}} [\phi^{-1} (7)^{\frac{1}{2}} Y_{43}^c + (\phi+3) Y_{41}^c] - \frac{4}{7} (5)^{-\frac{1}{2}} Y_{21}^c \}$
	$\psi_{22}^{(e)} = R_{22} \frac{1}{8} (455)^{\frac{1}{2}} \{ 5 (1183-273\phi)^{-\frac{1}{2}} [\frac{1}{2} (4\phi+1) (\frac{3}{2})^{\frac{1}{2}} Y_{65}^s + \frac{1}{22} (\frac{5}{2})^{\frac{1}{2}} (19-12\phi) Y_{63}^s - \frac{1}{2} Y_{61}^s] +$ $+ \frac{2}{77} (6)^{-\frac{1}{2}} [\phi (7)^{\frac{1}{2}} Y_{43}^s + (4-\phi) Y_{41}^s] - \frac{4}{7} (5)^{-\frac{1}{2}} Y_{21}^s \}$

Table 3. Zero-order eigenfunctions for H_g vibrations of I_h molecules

State	Eigenfunction
$ 0,0\rangle A_g$	$\psi_{00} = R_{00}Y_{00}$
$ 1,2\rangle H_g$	$\psi_{11}^{(a)} = R_{11}Y_{22}^c$; $\psi_{11}^{(b)} = R_{11}Y_{22}^s$; $\psi_{11}^{(c)} = R_{11}Y_{21}^c$; $\psi_{11}^{(d)} = R_{11}Y_{21}^s$; $\psi_{11}^{(e)} = R_{11}Y_{20}$
$ 2,0\rangle A_g$	$\psi_{20} = R_{20}Y_{00}$
$ 2,2\rangle H_g$	$\psi_{22}^{(a)} = R_{22}Y_{22}^c$; $\psi_{22}^{(b)} = R_{22}Y_{22}^s$; $\psi_{22}^{(c)} = R_{22}Y_{21}^c$; $\psi_{22}^{(d)} = R_{22}Y_{21}^s$; $\psi_{22}^{(e)} = R_{22}Y_{20}$
$ 2,4\rangle G_g$	$\psi_{22}^{(p)} = R_{22}(\frac{7}{12})^{\frac{1}{2}}\{(\frac{5}{7})^{\frac{1}{2}}Y_{44}^c + Y_{40}\}$; $\psi_{22}^{(q)} = R_{22}(\frac{7}{24})^{\frac{1}{2}}\{(2+\phi^{-2})(7)^{-\frac{1}{2}}Y_{43}^s - \phi Y_{41}^s\}$ $\psi_{22}^{(r)} = R_{22}(\frac{7}{24})^{\frac{1}{2}}\{-(2+\phi^2)(7)^{-\frac{1}{2}}Y_{43}^c + \phi^{-1}Y_{41}^c\}$; $\psi_{22}^{(s)} = R_{22}(\frac{1}{12})^{\frac{1}{2}}\{(5)^{\frac{1}{2}}Y_{44}^s + (7)^{\frac{1}{2}}Y_{42}^s\}$
$ 2,4\rangle H_g$	$\psi_{22}^{(a)'} = R_{22}(\frac{1}{12})^{\frac{1}{2}}\{-(7)^{\frac{1}{2}}Y_{44}^c + (5)^{\frac{1}{2}}Y_{40}\}$; $\psi_{22}^{(b)'} = R_{22}Y_{42}^{-c}$ $\psi_{22}^{(c)'} = R_{22}(\frac{1}{24})^{\frac{1}{2}}\{-(7)^{\frac{1}{2}}\phi Y_{43}^s - (3-\phi^{-1})Y_{41}^s\}$; $\psi_{22}^{(d)'} = R_{22}(\frac{1}{24})^{\frac{1}{2}}\{\phi^{-1}(7)^{\frac{1}{2}}Y_{43}^c + (3+\phi)Y_{41}^c\}$ $\psi_{22}^{(e)'} = R_{22}(\frac{5}{12})^{\frac{1}{2}}\{(\frac{7}{5})^{\frac{1}{2}}Y_{44}^s - Y_{42}^s\}$

Such splitting have been confirmed by calculating the perturbations produced by the anharmonicity (11) in the different vibrational levels. Thus, it has been sufficient in all cases under consideration to calculate the first order correction alone. Higher order perturbations, apart from being of a lesser magnitude than the former ones, do not produce any further splitting out merely confine themselves to displacing the previously split levels.

First order perturbation of the βr^4 and γr^6 terms achieves only a splitting of vibrational levels in the spherical symmetry, but their corrections will have to be born in mind since their magnitudes are important in the calculations. All the splitting inherent in the icosahedral symmetry is achieved when the corrections produced by the first order perturbations of the term $\gamma r^6 \{(105/22)^{\frac{1}{2}} Y_{66}^c - (7)^{\frac{1}{2}} Y_{64}^c - (21/2)^{\frac{1}{2}} Y_{62}^c + Y_{60}\}$ are introduced into the energy values.

The calculation of perturbed energies have only been made up to $v = 3$ for the T_{1u} vibrations, and up to $v = 2$ for the G_u and H_g vibrations because at and beyond these levels the splitting inherent to the icosahedral anisotropy is observable.

In Table 4 the expression obtained for the perturbed energies of the stationary states of the T_{1u} vibrations of I_h molecules and, as a part of them, the ones corresponding to the D_{1u} vibrations of the sphere are shown. As can be observed on descending in symmetry from K_h to I_h , the state $|3,3\rangle D_{3u}$ of the second overtone of K_h is split into states $|3,3\rangle T_{2u}$

Table 4. *Energies for the perturbed levels of T_{1u} vibrations of I_h molecules*

State		Energy
K_h	I_h	
$ 0,0\rangle D_{0g}$	$ 0,0\rangle A_g$	$\frac{3}{2} h\nu + \frac{15}{4} \beta + \frac{105}{8} \gamma$
$ 1,1\rangle D_{1u}$	$ 1,1\rangle T_{1u}$	$\frac{5}{2} h\nu + \frac{35}{4} \beta + \frac{315}{8} \gamma$
$ 2,0\rangle D_{0g}$	$ 2,0\rangle A_g$	$\frac{7}{2} h\nu + \frac{75}{4} \beta + \frac{945}{8} \gamma$ [$\gamma'' = (\frac{13}{\pi})^{\frac{1}{2}} \gamma'$]
$ 2,2\rangle D_{2g}$	$ 2,2\rangle H_g$	$\frac{7}{2} h\nu + \frac{63}{4} \beta + \frac{693}{8} \gamma$
$ 3,1\rangle D_{1u}$	$ 3,1\rangle T_{1u}$	$\frac{9}{2} h\nu + \frac{119}{4} \beta + \frac{1827}{8} \gamma$
	$ 3,3\rangle T_{2u}$	$\frac{9}{2} h\nu + \frac{99}{4} \beta + \frac{1287}{8} \gamma - 60\gamma''$
$ 3,3\rangle D_{3u}$	$ 3,3\rangle G_u$	$\frac{9}{2} h\nu + \frac{99}{4} \beta + \frac{1287}{8} \gamma + 45\gamma''$

Table 5. *Energies for the perturbed levels of H_g vibrations of I_h molecules*

State		Energy
K_h	I_h	
$ 0,0\rangle D_{0g}$	$ 0,0\rangle A_g$	$\frac{5}{2} h\nu + \frac{35}{4} \beta + \frac{315}{8} \gamma$
$ 1,2\rangle D_{2g}$	$ 1,2\rangle H_g$	$\frac{7}{2} h\nu + \frac{63}{4} \beta + \frac{693}{8} \gamma$
$ 2,0\rangle D_{0g}$	$ 2,0\rangle A_g$	$\frac{9}{2} h\nu + \frac{119}{4} \beta + \frac{1827}{8} \gamma$
$ 2,2\rangle D_{2g}$	$ 2,2\rangle H_g$	$\frac{9}{2} h\nu + \frac{99}{4} \beta + \frac{1287}{8} \gamma$
	$ 2,4\rangle G_g$	$\frac{9}{2} h\nu + \frac{99}{4} \beta + \frac{1287}{8} \gamma + 45\gamma''$
$ 2,4\rangle D_{4g}$	$ 2,4\rangle H_g$	$\frac{9}{2} h\nu + \frac{99}{4} \beta + \frac{1287}{8} \gamma - 36\gamma''$

and $|3,3\rangle G_u$ with contributions of $-60\gamma''$ and $45\gamma''$ and relative weights of 3 and 4, respectively. Thus it can be seen how the “centre of gravity” or “centre of energies” is maintained.

In Table 5 the perturbed energies corresponding to the H_g vibrations of I_h molecules and the D_{2g} of the sphere are shown. On descending in symmetry from K_h to I_h , the state $|2,4\rangle D_{4g}$ of the first overtone of K_h is split into the states $|2,4\rangle G_g$ and $|2,4\rangle H_g$ with contributions of $45\gamma''$ and $-36\gamma''$ and relative weights of 4 and 5, respectively, maintaining once again the “centre of gravity”.

In Table 6 the perturbed energies for the G_u vibrations of I_h molecules are shown. In this case the “centre of gravity” is not maintained since, as we said before, the parentage of these vibrations with progenitors D_{3u} of K_h is of a fractional type. In fact, each state of I_h in a particular level $|\nu\rangle \Gamma$ comes from the partial contributions of the different states of such levels in K_h .

We have also calculated the perturbed eigenfunctions of the T_{1u} vibrations of I_h , bearing in mind the first order corrections introduced by

Table 6. Energies for the perturbed levels of G_u vibrations of I_h molecules

State	Energy
$ 0\rangle A_g$	$2 h\nu + 6 \beta + 24 \gamma$
$ 1\rangle G_u$	$3 h\nu + 12 \beta + 60 \gamma + \frac{2400}{143} \gamma''$
$ 2\rangle A_g$	$4 h\nu + 24 \beta + 168 \gamma + \frac{21840}{323} \gamma''$
$ 2\rangle G_g$	$4 h\nu + 20 \beta + 120 \gamma + \frac{19200}{323} \gamma''$
$ 2\rangle H_g$	$4 h\nu + 20 \beta + 120 \gamma + \frac{146400}{3553} \gamma''$

Table 7. Perturbed eigenfunctions for T_{1u} vibrations of I_h molecules

State	Eigenfunction
$ 0, 0\rangle A_g$	$\psi_{00} = \psi_{00} + \frac{5}{4}(6)^{\frac{1}{2}}b \psi_{20} - \frac{1}{8}(30)^{\frac{1}{2}}b \psi_{40}$
$ 1, 1\rangle T_{1u}$	$\psi_{11}(x, y, z) = \psi_{11}(x, y, z) + \frac{7}{4}(10)^{\frac{1}{2}}b \psi_{31}(x, y, z) - \frac{1}{8}(70)^{\frac{1}{2}}b \psi_{51}(x, y, z)$
$ 2, 0\rangle A_g$	$\psi_{20} = \psi_{20} - \frac{5}{4}(6)^{\frac{1}{2}}b \psi_{00} + \frac{9}{2}(5)^{\frac{1}{2}}b \psi_{40} - \frac{1}{8}(210)^{\frac{1}{2}}b \psi_{60}$
$ 2, 2\rangle H_g$	$\psi_{22}(a, b, c, d, e) = \psi_{22}(a, b, c, d, e) + \frac{9}{4}(14)^{\frac{1}{2}}b \psi_{42}(a, b, c, d, e) - \frac{3}{8}(14)^{\frac{1}{2}}b \psi_{62}(a, b, c, d, e)$
$ 3, 1\rangle T_{1u}$	$\psi_{31}(x, y, z) = \psi_{31}(x, y, z) - \frac{7}{4}(10)^{\frac{1}{2}}b \psi_{11}(x, y, z) + \frac{11}{2}(7)^{\frac{1}{2}}b \psi_{51}(x, y, z) - \frac{3}{8}(42)^{\frac{1}{2}}b \psi_{71}(x, y, z)$
$ 3, 3\rangle T_{2u}$	$\psi_{33}(i, j, k) = \psi_{33}(i, j, k) + \frac{33}{4}(2)^{\frac{1}{2}}b \psi_{53}(i, j, k) - \frac{3}{8}(22)^{\frac{1}{2}}b \psi_{73}(i, j, k)$
$ 3, 3\rangle G_u$	$\psi_{33}(p, q, r, s) = \psi_{33}(p, q, r, s) - \frac{3}{8}(22)^{\frac{1}{2}}b \psi_{73}(p, q, r, s)$
	$b = \frac{\beta}{h\nu}$

the term βr^4 of (11), which are of great magnitude. Thus we have obtained perturbed eigenfunctions up to $v = 3$. The results obtained appear in Table 7.

Finally, we calculated expressions for the intensity of the vibrational T_{1u} transitions of I_h molecules active in the infrared, using the perturbed eigenfunctions calculated above.

We made these intensity calculations using *Einstein's* coefficients defined as:

$$B_{nm} = \frac{8\pi^3}{3h^2} \frac{g_m}{g_n} \langle \Psi_m | \hat{\mu} | \Psi_n \rangle^2 \quad (12)$$

where g_m and g_n are the degeneracies of the upper and lower levels of the corresponding transitions and $\hat{\mu}$ is the dipolar moment operator. To evaluate the matrix elements $\langle \Psi_m | \hat{\mu} | \Psi_n \rangle^2$, or transition moment, we broke the dipole moment operator, $\hat{\mu}$, into its three components $\{\mu_x, \mu_y, \mu_z\}$. We

expanded each of them in power series, bearing in mind that each term of that expansion has to be a basis of the same representation to which the set of coordinates $\{x, y, z\}$ is associated. The expression of these components of the dipole moment in a linear combination of spherical harmonics is given by:

$$\begin{aligned} \mu_x &= \mu \left(\frac{4\pi}{3} \right)^{1/2} r Y_{11}^c + \mu \frac{21(2)^{-1/2}}{4} r^5 \left\{ \frac{(3\phi - 1)}{6(14)^{1/2}} Y_{55}^c - \frac{\phi^{-1}(14)^{1/2}}{28} Y_{53}^c - \frac{(\phi - 3)(3)^{1/2}}{42} Y_{51}^c \right\} + \dots \\ \mu_y &= \mu \left(\frac{4\pi}{3} \right)^{1/2} r Y_{11}^s + \mu \frac{21(2)^{-1/2}}{4} r^5 \left\{ \frac{(2 - 3\phi)}{6(14)^{1/2}} Y_{55}^s + \frac{\phi(14)^{1/2}}{28} Y_{53}^s + \frac{(4 - \phi)(3)^{1/2}}{42} Y_{51}^s \right\} + \dots \\ \mu_z &= \mu \left(\frac{4\pi}{3} \right)^{1/2} r Y_{10} + \mu \frac{21(2)^{-1/2}}{4} r^5 \left\{ -\frac{5(35)^{-1/2}}{6} Y_{54}^c - (21)^{-1/2} Y_{52}^c - \frac{1}{14} Y_{50} \right\} + \dots \end{aligned} \quad (13)$$

From these expressions we have only retained the contributions given by the first terms, since those given by the second ones are four orders of magnitude less than these of the first ones.

In this way we have calculated *Einstein's* absorption coefficients, B_{nm} , for the fundamental and the second overtone transitions, obtaining the results shown in Table 8.

Table 8. *Einstein's coefficients of T_{1u} vibrations of I_h molecules*

Transition	$B_{nm} \text{ (m}^3\text{s}^{-1}\text{molec}^{-1}\text{)} \cdot 10^{-6}$
$ 1, 1\rangle_{T_{1u}} - 0, 0\rangle_{A_g}$	$\frac{4\pi^3}{h} \left(1 - \frac{5}{2}b\right)^2 \mu^2$
$ 3, 1\rangle_{T_{1u}} - 0, 0\rangle_{A_g}$	$\frac{15\pi^3}{2h^2} b^2 \mu^2$

$b = \frac{\beta}{h\nu}$

All the radial matrix elements necessary to our calculations have been evaluated according to *Shaffer* [15] and *Shaffer et al.* [19]; nevertheless, we had to evaluate the angular matrix elements ourselves.

Conclusion

In conclusion we feel able to say that we have obtained all the splitting predicted by the group theory for the overtone levels of the T_{1u} , G_u and H_g vibrations of molecules with I_h symmetry; in the first case up to $v = 3$ and in the rest up to $v = 2$. To achieve this we had to establish the sixth power

icosahedral potential beforehand, employing the usual procedure in crystal field theory. We also had to elaborate zero order eigenfunctions consisting of a radial part, which will be that of the isotropic harmonic oscillator in three-, four- and five-dimensions, depending on whether they are T_{1u} , G_u and H_g vibrations, and symmetry-adapted angular parts. Furthermore, we have obtained expressions for *Einstein's* coefficients, B_{nm} , of the active transitions in infrared for T_{1u} vibrations of molecules with I_h symmetry.

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