

The IR and Raman activities of the icosahedral molecule

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This paper describes the selection rules for the IR and Raman activities of the icosahedral molecule. The tensor expressions are given for the effective charge and Raman tensors, and their symmetry properties are discussed. The tensor expression is inevitable, in particular, for homopolar molecules and elementary crystals. This paper also provides the specific characteristics of the well-known models of vibrations, such as the shell model, the bond-charge model, and the bond-polarizability model.

I. INTRODUCTION

In this paper, I present mathematical formulae to describe IR and Raman activities for molecules having icosahedral symmetry. For the Raman tensors, the form of the second-rank tensors are tabulated for all the crystallographic point groups in textbooks [1]. There is, however, no description for the I_h symmetry. To write it down may be worthwhile.

Special attention will be paid to those solids, which are composed of only one chemical species. In the static sense, these solids are not able to have dipole moment. In spite of this, many solids of this type have IR active vibrations. In the crystal case (elemental crystals), the following criterion holds [2],

Elementary crystals which have more than two atoms in the primitive cell necessarily have at least one IR-active mode. (a)

In the same line of argument as in Ref. 2, we can reach the following conclusion for homopolar molecules,

Homopolar molecules which are composed of more than two atoms necessarily have at least one IR-active mode. (b)

The dynamic and distortion effect of the charge distribution is the cause of this IR activity [2-4]. Without use of the tensor expression, we could not describe the IR activity for these solids. The symmetry properties of these tensors will be discussed.

This paper gives also the specific features of the IR and Raman activities, which are obtained when using a special model of vibrations, such as the shell model (SM), the bond-charge model (BCM), and the bond-polarizability model.

This paper assumes a molecule for a substance. However, most of the results can be applied to crystals, so that the terms of molecule and primitive unit cell will be used interchangeably. The simplest icosahedral molecule is that the molecule has 12 atoms at each vertex (Fig. 1). The symmetry decomposition of the vibrations is as follows; $A_g + T_{1g} + 2T_{1u} + T_{2u} + U_g + U_u + 2V_g + V_u$, where T_{1u} is IR-active while A_g and V_g are Raman active. Throughout this paper, a five-fold axis is taken as the z-axis. It should be noted that the present coordinates system is different from the previous ones in Ref. 4, and accordingly so is the tensor expressions.

II. EFFECTIVE CHARGE TENSORS

The first-order dipole moment \mathbf{p} induced by a vibration is expressed by the effective charge tensor \mathbf{B}^κ of κ -th atom as [2,5],

$$\mathbf{p} = \sum_{\kappa} \mathbf{B}^\kappa \mathbf{u}_\kappa. \quad (1)$$

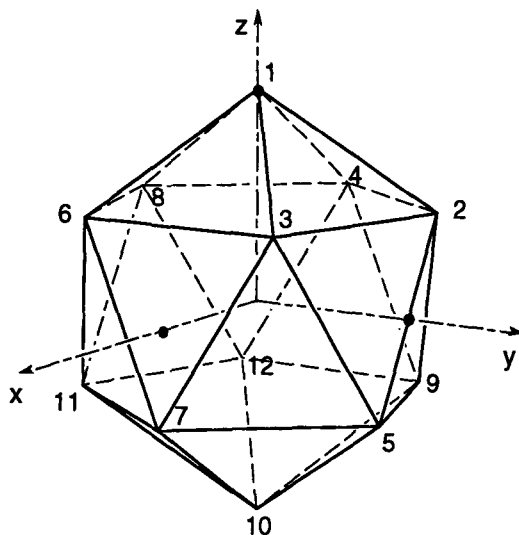


Fig. 1 The geometry of the icosahedron and the coordinates system.

There are $3 \times 3s$ coefficients $B_{\alpha\beta}^{\kappa}$ in all, where s is the number of atoms in the primitive unit cell. Among them, only the number of components as many as the number of the polar vibrations are non-zero, and only the number of them as many as the number of the distinct frequencies are independent.

The second-rank tensor \mathbf{B}^{κ} is subject to the symmetry of the system [5,6]. Every component must satisfy the transformation relations

$$\mathbf{B}^{\kappa} = \mathbf{S} \mathbf{B}^{\kappa(\circ)S}, \quad (2)$$

for the space group operations ($S|v$). The translational invariance leads to the second requirement of the charge neutrality,

$$\sum_{\kappa} \mathbf{B}^{\kappa} = 0. \quad (3)$$

Two requirements (2) and (3) determine the symmetry properties of \mathbf{B}^{κ} completely. For elemental crystals $s = 2$, it has been proven that there is necessarily the inversion element, by which the two basis atoms are interchanged each other [2], leading an equality $\mathbf{B}^2 = \mathbf{B}^1$. With help of (3), this leads to the conclusion that all effective charges vanish in this case, which agrees with the IR experiment. For a general case of elemental crystals ($s > 3$), even if the crystal has inversion, such cancellation does not occur.

In this way, an icosahedral molecule has non-zero effective charges. In the special case of the simplest icosahedral molecule, the number of independent components is only one (T_{1u}). An expression of the effective charge tensors is given in Ref. 4. Since a different coordinate system was used there, I again record here another expression in the current coordinates system,

$$\mathbf{B}^1 = \begin{bmatrix} \frac{1}{2} & 0 & 0 \\ & \frac{1}{2} & 0 \\ & & -1 \end{bmatrix}, \quad \mathbf{B}^4 = \begin{bmatrix} -\frac{7}{10} & 0 & \frac{3}{5} \\ & \frac{1}{2} & 0 \\ & & \frac{1}{5} \end{bmatrix},$$

$$\mathbf{B}^2 = \begin{bmatrix} \frac{1+3\sqrt{5}}{20} & \frac{3\sqrt{5}-\sqrt{5}}{10\sqrt{2}} & \frac{3(-1+\sqrt{5})}{20} \\ & -\frac{5+3\sqrt{5}}{20} & -\frac{3\sqrt{5}+\sqrt{5}}{10\sqrt{2}} \\ & & \frac{1}{5} \end{bmatrix}$$

(4)

neglecting a common factor. In addition to usual symmetry requirements 2 and 3, $\text{Tr } \mathbf{B}^{\kappa} = 0$ also holds.

If this icosahedron is deformed, the crystal symmetry is lowered, and more numbers of independent components of $B_{\alpha\beta}^{\kappa}$ appear. Let demonstrate how to count the number, by taking as instance the deformation to D_{3d} , like α -rhombohedral boron [4]. The requirement for the rotational invariance, Eq. (2), reduces the number of the independent components to 10. This can be checked by using the characters χ_{tot} of the D_{3d} representation in the 108-dimensional space spanned by $B_{\alpha\beta}^{\kappa}$. The number of independent com-

ponents of $B_{\alpha\beta}^{\kappa}$ is obtained by $(1/h) \sum N(R) \chi_{\text{at}}(S)$, where $\chi_{\text{at}}(S)$ is the character of the representation of a 9-dimensional subspace $B_{\alpha\beta}^{\kappa}$ for a fixed atom κ which position is invariant under a rotational operation S , and $N(S)$ is the number of such atoms. Only operations having non-zero $N(S)$ are the identity E and three mirror reflections σ_d .

$\chi_{\text{at}}(\sigma_d)$ is 1, because five components of the $B_{\alpha\beta}^{\kappa}$ for a fixed κ are invariant under a mirror reflection while the remaining four change the sign with no change in the suffices. $(1/h) \sum N(S) \chi_{\text{at}}(S)$ is then computed to be $[1 \cdot 12 \cdot \chi_{\text{at}}(E) + 3 \cdot 4 \cdot \chi_{\text{at}}(\sigma_d)] / 12 = 10$. The translational invariance requirement Eq. (3) further imposes two conditions, say, with respect to the x - and z -directions, leaving 8 independent components. The final expressions of the effective charge tensors have 8 independent parameters, which agrees with the number of the polar vibrations of this deformed icosahedron.

Model calculation

So far, no specific model has been assumed. The value of the effective charge can be obtained by using a model. The SM and the BCM are the ones which are commonly used. The effective charge of the simplest icosahedral molecule has been calculated by these two models [4,7]. Difference between the two models is usually not significant, as far as the zone-center frequencies are concerned. However, it is interesting to point out that different models make a significant consequence on the effective charge for the special type molecule [7].

In terms of the SM, non-vanishing dipole moment arises from the uniformly translational motions of elec-

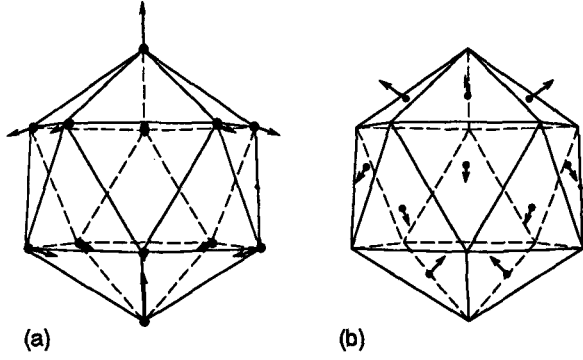


Fig. 2 The shell motions s_2 for T_{1u} mode (a) in the SM and (b) in the BCM.

trons. The coupling of this component (s_1 type) of the electron motion to the polar vibration of cores (c_2 type) determines the magnitude of the effective charge. The coupling coefficient a_{12} is determined by requiring for the electron displacement to minimize the deformation potential for the core displacement of the type c_2 . The displacements of the s_2 type in the SM and BCM are depicted in Fig. 2. In the SM, it is quite plausible that a_{12} is small. In this model, each electron definitely belongs to an atom, and the displacement of the electron relative to that of the core is not significant. A large a_{12} implies a large component of s_1 type, which would cause the deformation energy increased considerably. In the BCM, on the other hand, the shell and

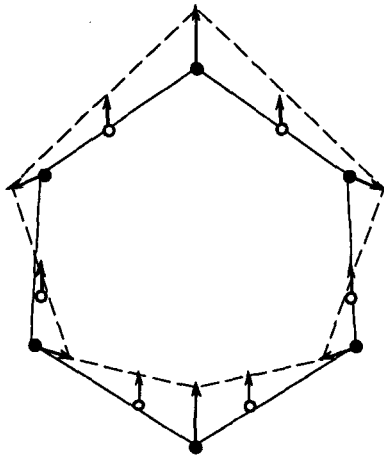


Fig. 3 The deformation of the icosahedron caused by the core motion c_2 naturally induces a uniformly translational motion of the bond charges

the core are separated from the beginning (in the present problem each bond charge is located at the center of a triangle), and there happens a special condition that the s_1

type motion makes the deformation energy minimized. Figure 3 shows that this special condition actually occurs. It is clear that coupling to the s_1 motion is energetically favorable, compared with the coupling to the s_2 motion. This special situation, however, brings another a subtle problem of the validity of the adiabatic approximation (see [7]).

III. RAMAN SCATTERING TENSORS

For Raman scattering, the coefficients of the scattering efficiency are also subject to the crystal symmetry. The form of the Raman tensor of first order can be obtained by the projection method as,

$$P(r)_{\alpha\beta,\mu} = \frac{l}{h} \sum_{S \in G} \Gamma_r(S)_{\mu\mu} G(S) P(r)_{\alpha\beta,\mu}, \quad (5)$$

where r denotes the label of the irreducible representation Γ , μ is the index of the partner, G is the operator of a rotation S [8]. Although the calculation is rather straightforward, the application of the projection operator means a number of operations as many as the order h of the group. In the present case, $h = 120$ thereby the calculation is a laborious task. Another method to obtain the form is use of the symmetry requirement [9],

$$P(r)_{\alpha\beta,\mu} = \sum_{\gamma\delta\nu} S_{\gamma\alpha} S_{\delta\beta} \Gamma_r(S)_{\nu\mu} P(r)_{\gamma\delta,\nu}. \quad (6)$$

In this case, all the partners must be considered simultaneously however. By using either way, the general form of the Raman tensors for I_h symmetry can be derived as,

$$P(Ag) = \begin{pmatrix} a & \cdot & \cdot \\ \cdot & a & \cdot \\ \cdot & \cdot & a \end{pmatrix},$$

$$P(Vg,1) = \begin{pmatrix} -b & \cdot & \cdot \\ \cdot & b & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}, \quad P(Vg,2) = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & b \\ \cdot & b & \cdot \end{pmatrix},$$

$$P(Vg,3) = \begin{pmatrix} \cdot & \cdot & b \\ \cdot & \cdot & \cdot \\ b & \cdot & \cdot \end{pmatrix}, \quad P(Vg,4) = \begin{pmatrix} \cdot & b & \cdot \\ b & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix},$$

$$P(Vg, 5) = \begin{pmatrix} -\frac{b}{\sqrt{3}} & \cdot & \cdot \\ \cdot & -\frac{b}{\sqrt{3}} & \cdot \\ \cdot & \cdot & \frac{2b}{\sqrt{3}} \end{pmatrix}, \quad (7)$$

Here, we assume that $P(r)_{\alpha\beta,\mu}$ is symmetric in α and β , which is valid when the frequency is far from the resonant condition. In obtaining this expression for V_g , use is made of the convention that the five partners are transformed as the following functions and in this order,

$$\begin{aligned} (1/2)(y^2-x^2), yz, zx, xy, \\ (1/2\sqrt{3})(2z^2-x^2-y^2). \end{aligned} \quad (8)$$

Model calculation

To obtain a concrete form of the Raman tensor, the bond polarizability model is often used [10,11]. In this model, the polarizability is given by the polarizabilities of the bonds, which comprise the molecule. The cylindrical symmetry is assumed with respect to the bond axis, so that two parameters, say transverse and longitudinal polarizabilities (α_{\perp} and α_{\parallel}), are involved. Furthermore, the change in the polarizabilities of bond depends only on the length of the bond R_b . On this assumption, the first-order polarizabilities are obtained as,

The prime stands for the derivative with respect to R_b . The summation is taken over all the bonds $b = (lm)$, which have

$$\mathbf{P}^{(1)} = \sum_b \left\{ \left[\alpha_{\parallel}(R)'(\hat{\mathbf{R}}_b \otimes \hat{\mathbf{R}}_b) + \alpha_{\perp}(R)'(1 - \hat{\mathbf{R}}_b \otimes \hat{\mathbf{R}}_b) \right] (\mathbf{R}_b \cdot \mathbf{u}_{lm}) + \frac{\alpha_{\parallel}(R) - \alpha_{\perp}(R)}{R_b} \left[\hat{\mathbf{R}}_b \otimes \mathbf{u}_{lm} + \mathbf{u}_{lm} \otimes \hat{\mathbf{R}}_b - 2 \hat{\mathbf{R}}_b \otimes \hat{\mathbf{R}}_b (\mathbf{R}_b \cdot \mathbf{u}_{lm}) \right] \right\}, \quad (9)$$

the unit vector $\hat{\mathbf{R}}_b$ pointing to atom m from l , and $\mathbf{u}_{lm} = \mathbf{u}_l - \mathbf{u}_m$. In the present problem of the simplest icosahedral molecule, the constants a and b in the Raman tensors (7) are obtained as,

$$\begin{aligned} a &= -\sqrt{\frac{10(5-\sqrt{5})}{3}} \{ \alpha_{\parallel}(R)' - \alpha_{\perp}(R)' \}, \\ b &= -\sqrt{\frac{3(5+\sqrt{5})}{10}} \left\{ \alpha_{\parallel}(R)' - \alpha_{\perp}(R)' - 2 \frac{\alpha_{\parallel}(R) - \alpha_{\perp}(R)}{R_b} \right\} \end{aligned} \quad (10)$$

The two bond polarizabilities enter the formulae only

through their difference. In the special case of spherical bonds, the scattering efficiencies will vanish accidentally.

I have obtained the above exact expressions, not floating-point expressions, by a symbolic calculation on Mathematica. The symbolic calculation enables us to obtain exact expressions for such a complicated system, which would be difficult otherwise.

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