

General Relations between the Symmetry of Molecules and their Vibrational Spectra

In the paper some relations between the symmetry of the polyatomic molecules and its spectra are given. Especially the mutual correspondences of 1) the decay of the vibrational representation (1) — which has a form (1a) and (1b) in the illustrative case of H₂O and N₂O₂, 2) the term of vibrational energy (3a) — e.g. (3b), (3c) for H₂O, and N₂O₂ — and 3) generalized selection rule (7) — especially (7d) for H₂O — are given. From this general selection rule follow well known selection rules for fundamental, harmonic and different frequencies as special cases, are shown.

The paper indicates some relations between the symmetry of polyatomic molecules and the vibrational spectra which can be used to generalizing the well known results for the case of the most general vibrational states and combinational frequencies. Independently their practical usage in infrared and Raman spectroscopy will be shown.

If we know the geometrical model of a tested *N*-atomic molecule and its group of symmetry *G*, than we can — having the tables of characters of irreducible representations [1] — make a decay (1) of the vibrational representation *D_v* to the direct sum of *n* irreducible representations *I*_{[*d_i]*}^(*i*) [2].

$$\begin{aligned} \text{Decay } D_v &= \sum_{i=1}^r n_i \Gamma_{[d_i]}^{(i)} \\ &\equiv n_1 \Gamma_{[d_1]}^{(1)} \oplus n_2 \Gamma_{[d_2]}^{(2)} \oplus \dots \oplus n_i \Gamma_{[d_i]}^{(i)} \oplus \dots \oplus \\ &\quad \oplus n_r \Gamma_{[d_r]}^{(r)}. \end{aligned} \quad (1)$$

The index in brackets [*d_i*] means the dimension of *I*^(*i*). For example the molecules H₂O (symmetry *C*_{2v}) and N₂O₂ (symmetry *C*_{2h}) have

$$\text{decay } D_v(X_2Y) = 2A_1 \oplus B_1, \quad (1a)$$

$$\text{decay } D_v(X_2Y_2) = 3A_g \oplus A_u \oplus 2B_u. \quad (1b)$$

It is evident that the decay (1) contains

$$n = \sum_{i=1}^r n_i \quad (2)$$

members in *r* various terms.

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The term of vibrational energy of the molecular oscillator is a function of just *n* vibrational quantum numbers *v_k*^(*i*)

$$\begin{aligned} E(v) &= E(v_1^{(1)}, v_2^{(1)}, \dots, v_{n_1}^{(1)}; \\ &\quad v_1^{(2)}, \dots, v_{n_2}^{(2)}; \dots, v_{n_r}^{(r)}) \end{aligned} \quad (3)$$

and has an approximate form

$$\begin{aligned} E(v) &\approx h \sum_{i=1}^n v_i \left(v_i + \frac{d_i}{2} \right) + \\ &+ \sum_{i=1}^n \sum_{k=1}^n \xi_{ik} \left(v_i + \frac{d_i}{2} \right) \left(v_k + \frac{d_k}{2} \right). \end{aligned} \quad (3a)$$

The symmetry properties of excited vibrational states are described by means of the product of the symmetrized powers of the irreducible representations which are presented in the decay (1) and whose exponents are equal to the values of the quantum numbers *v_k*^(*i*), i.e.

$$D(v) = \prod_{i=1}^r \prod_{k=1}^{n_i} [\Gamma_k^{(i)}]^{v_k}. \quad (4)$$

In the simple case of molecule H₂O and N₂O₂ the term (3) and the product of irreducible representations (4) has a form

$$\begin{aligned} E(v) &\equiv E(v_1^{(1)}, v_2^{(1)}; v_1^{(2)}) \approx h \left[v_1 \left(v_1^{(1)} + \frac{1}{2} \right) + v_2 \left(v_2^{(1)} + \frac{1}{2} \right) + v_3 \left(v_1^{(2)} + \frac{1}{2} \right) \right] + \text{quadratic terms}, \end{aligned} \quad (3b)$$

$$E(v) \equiv E(v_1^{(1)}, v_2^{(1)}, v_3^{(1)}; v_1^{(2)}; v_1^{(3)}, v_2^{(3)})$$

$$\approx h \left[v_1 \left(v_1^{(1)} + \frac{1}{2} \right) + v_2 \left(v_2^{(1)} + \frac{1}{2} \right) + v_3 \left(v_3^{(1)} + \frac{1}{2} \right) + v_4 \left(v_1^{(2)} + \frac{1}{2} \right) + v_5 \left(v_1^{(3)} + \frac{1}{2} \right) + v_6 \left(v_2^{(3)} + \frac{1}{2} \right) \right] +$$

+ quadratic terms, (3c)

$$D(v) = [A_1]^{v_1^{(1)}} \otimes [A_1]^{v_2^{(1)}} \otimes [B_1]^{v_1^{(2)}}, \quad (4a)$$

$$D(v) = [A_g]^{v_1^{(1)}} \otimes [A_g]^{v_2^{(1)}} \otimes [A_g]^{v_3^{(1)}} \otimes [A_u]^{v_1^{(2)}} \otimes [B_u]^{v_1^{(3)}} \otimes [B_u]^{v_2^{(3)}}. \quad (4b)$$

If the transformational properties of the molecular dipole momentum components P_i and of the tensor of polarizability components α_{ik} (i and $k = x, y, z$) are known and described by means of the irreducible representations $\sim(P_i)$ and $\sim(\alpha_{ik})$ then the next general selection rule is applicable:

The frequency ν of the molecular vibrations

$$\nu = \frac{1}{h} |E(v) - E(v')|, \quad (5)$$

which is usually denoted in spectroscopy as a frequency of the type

$$\left| \sum_{i=1}^r \sum_{k=1}^{n_2} (v_k^{(i)} - v_k^{(i')}) \nu_k^{(i)} \right| \quad (5a)$$

corresponding to the transition

$$D(v) - D(v') \quad (6)$$

which is infrared or Raman active if and only if the

$$\text{decay } \{D(v) \otimes D(v')\} \supset \sim(P_i) \text{ or } \sim(\alpha_{ik}) \quad (7)$$

respectively.

For the simple case of the H_2O molecule the expression $D(v) \otimes D(v')$ has the following form

$$D(v) \otimes D(v') = [A_1]^{v_1^{(1)}} \otimes [A_1]^{v_2^{(1)}} \otimes [B_1]^{v_1^{(2)}} \otimes [A_1]^{v_1^{(1)'}} \otimes [A_1]^{v_2^{(1)'}} \otimes [B_1]^{v_1^{(2)'}}. \quad (7a)$$

Because for each integer number $v_k^{(i)}$ is identical,

$[A_1]^{v_k} = A_1$ and it is sufficient to consider only the expression

$$B_1^{v_1^{(2)}} \otimes B_1^{v_1^{(2)'}} \quad (7b)$$

from the (7a). The product (7b) equals either A_1 or B_1 depending on whether the value of the sum $v_1^{(2)} + v_1^{(2)'}$ is even or odd. The product (7a) is equal

$$D(v) \otimes D(v') \begin{cases} A_1 \\ B_1 \end{cases} \quad (7c)$$

at least.

In order to form the selection rule (7) it is useful to remember that according to A_1 representation the P_z component of dipole momentum is transformed and so are the components α_{xx} , α_{yy} , α_{zz} of the polarizability tensor; these facts being written down as follows

$$A_1(P_z; \alpha_{xx}, \alpha_{yy}, \alpha_{zz})$$

and

$$B_1(P_x; \alpha_{xz}).$$

Therefore, it is clear that the decay

$$D(v) \otimes D(v')$$

$$\supset A_1(P_z; \alpha_{xx}, \alpha_{yy}, \alpha_{zz}) \text{ or } B_1(P_x; \alpha_{xz}) \quad (7d)$$

and this is why all of the vibrational frequencies

$$\nu = \frac{1}{h} |E(v_1^{(1)}, v_2^{(1)}; v_2^{(2)}) - E(v_1^{(1)'}, v_2^{(1)'}; v_1^{(2)'})|$$

in spectroscopy usually signed by

$$|v_1^{(1)} \nu_1(A_1) + v_2^{(1)} \nu_2(A_1) + v_1^{(2)} \nu_3(B_1) - v_1^{(1)'} \nu_1(A_1) - v_2^{(1)'} \nu_2(A_1) - v_1^{(2)'} \nu_3(B_1)|$$

are both infrared and Raman active according to (7). As a trivial consequence from above it follows that all of the fundamental, harmonic, different and combinational frequencies are active in infrared and Raman spectrum.

Relations générales entre la symétrie des molécules et leurs spectres de vibration

On s'occupe, dans cet article, de certaines relations entre la symétrie des molécules polyatomiques et les spectres de vibration par la généralisation de résultats connus, concernant les états de vibration les plus généraux et les combinaisons de fréquences. On indique également leur utilisation pratique à la spectroscopie infrarouge et Raman.

Общие соотношения между симметрией молекул и их вибрационными спектрами

В статье обсуждаются некоторые соотношения между симметрией многоатомных молекул и вибрационными спектрами по отношению к обобщениям хорошо известных результатов, касающихся наиболее вибрационных состояний и комбинационных частот. Указывается также их практическое применение в инфракрасной и рамановой спектроскопии.

References

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