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VIBRATIONAL ENERGY OF LINEAR MOLECULES AND ALLOWED TRANSITIONS IN INFRARED AND RAMAN SPECTRA

VLADIMÍR MALÍŠEK

1. INTRODUCTION

The idea of a possible use of the representation theory of group symmetry for the study of vibrational spectra of molecules is of old-standing [5], [29]. But for all that no sufficient attention has been given to the general formulation of relations between the quantum-mechanical and the group-theoretical parameters of the vibrational state of a molecule in the above mentioned papers nor in the recent works [6], [13], [24], either.

This paper is devoted to some mechanical and group-theoretical characteristics of the vibrational state of a molecule, especially to:

a) the description of vibrational state by means of symmetrical powers of the irreducible representations;

b) the formulation of general selection rules in infrared and Raman spectra;

c) the illustration of a general way for the case of linear molecules. Their symmetry is characterized either by a group of symmetry $\mathbf{C}_{\infty v}$ (if the centre of symmetry is absent) or by $\mathbf{D}_{\infty v}$ (if the molecule possesses the centre of symmetry). Linear molecules are not only theoretically interesting (infinite groups are the matter), but they are of great practical importance as well. For example molecules XY (*HF, TF, HCl, TCl, HBr, TBrHI, NO, CO*) and XYZ molecules (*HCN, TCN, FCN, ClCN, BrCN, ICN, SCO, SCSe, SCTe*) belong to the symmetry $\mathbf{C}_{\infty v}$; the $\mathbf{D}_{\infty h}$ symmetry appears in cases of $X_2(H_2, D_2, O_2, N_2)$, $X_3(C_3$ in C_3O_2, N_3 in $KN_3)$ and *YXY(HCN, TCN, FCN, ClCN, BrCN, ICN, SCOSCSe, SCTe)* molecules.

2. A CHARACTERISTIC OF VIBRATIONAL STATE AND OF ENERGY TRANSITIONS IN THE CASE OF A GENERAL N-ATOMIC MOLECULE

There result some important facts about the vibrational state of a general N-atomic molecule of the G-symmetry from the splitting of its D_0 vibrational representation into the direct sum of irreducible representations $\Gamma_{d_i}^{(i)}$ of the **G** group

$$D_0 = n_1 \Gamma_{d_1}^{(1)} \oplus n_2 \Gamma_{d_2}^{(2)} \oplus \ldots \oplus n_i \Gamma_{d_i}^{(i)} \oplus \ldots \oplus n_r \Gamma_{d_r}^{(r)}, \tag{1}$$

where d_i is the dimension of the i-th irreducible representation $\Gamma_{d_i}^{(i)}$. As to each term $n_i \Gamma_{d_i}^{(i)}$ in (1) corresponds the number n_i of vibrational quantum numbers $v_1^{(i)}, v_2^{(i)}, \ldots, v_{n_i}^{(i)}$, it is suitable to denote the corresponding quantum numbers by the common index (i). Therefore, unlike the general practice, the designation of quantum number by two indices $v_j^{(i)}$ is used which indicate that the j-th quantum number from the quantum number set corresponding to the irreducible representation $\Gamma_{d_i}^{(i)}$ is in question. On the basis of quantum mechanics and the splitting (1) it is possible to characterize the vibrational state of a molecule without solving the problem of molecular vibrations [19] as follows:

1. A linear or non-linear molecule has s degrees of freedom, whereby

$$s = 3N - 5, \quad \text{or} \quad s = 3N - 6. \tag{2}$$

Thus it can carry out s normal oscillations and there exists a one-to-one correspondence between the mechanical oscillations and the irreducible representations in the splitting (1).

2. That is to say that to each term $n_i \Gamma_{d_i}^{(i)}$ in (1) correspond n_i different frequencies $v_1^{(i)}$, $v_2^{(i)}, \ldots v_{n_i}^{(i)}$, each of which is d_i-fold (i.e. d_i-times degenerate), which means, that to each of the introduced frequencies correspond d_i of different normal oscillations. Consequently the total number of the normal oscillations equals to

$$s = \sum_{i=1}^{r} n_i d_i \tag{3}$$

and the total number of the mutually different normal frequencies equals to

$$n = \sum_{i=1}^{r} n_i, \tag{4}$$

3. The term of vibrational energy of a molecule is a function of n normal frequences $v_j^{(i)}$ and a function of n quantum numbers bearing the form

$$E(v) = \sum_{i=1}^{r} \left[\sum_{k=1}^{n_i} v^{(i)} \left(v_k^{(i)} + \frac{d_i}{2} \right) \right] + \sum_{\substack{i,j=1 \\ (i \geqq j)}}^{r} \left[\sum_{k=1}^{n_i} \sum_{l=1}^{n_j} x_{kl}^{(ij)} \left(v_k^{(i)} + \frac{d_i}{2} \right) \left(v_l^{(j)} + \frac{d_j}{2} \right) \right]. \tag{5}$$

4. The vibrational state of the molecule is described by the vector $| v >$ having also n components collected in r sets

$$| v > = | v_1^{(1)}, v_2^{(1)}; \ldots, v_{n_1}^{(1)}; \ldots, v_1^{(i)}, v_2^{(i)}, \ldots; v_{n_i}^{(i)}; \ldots; v_1^{(r)}, v_2^{(r)}, \ldots; v_{n_r}^{(r)} \rangle. \tag{6}$$

5. The symmetry of the general vibrational state (6) of the molecule is characterized by the product $D(v)$ of symmetrical powers of irreducible representations (7)

$$D(v) = D_1 \otimes D_2 \otimes \ldots \otimes D_i \otimes \ldots \otimes D_r. \tag{7}$$

and

$$D_i = \left[\Gamma_{d_i}^{(i)}\right]^{v_1^{(i)}} \otimes \left[\Gamma_{d_i}^{(i)}\right]^{v_2^{(i)}} \otimes \ldots \otimes \left[\Gamma_{d_i}\right]^{v_{n_i}^{(i)}}. \tag{8}$$

In the expression (7) there are symmetrical powers of all irreducible representations contained in the splitting (1). In special cases it is easy to split the products (7) and (8) by means of the tables for products of irreducible representations and symmetrical powers of irreducible representations contained e.g. in [12], [13] etc.

6. The frequency corresponding to the transition

$$\left(v_1^{(1)}, v_2^{(1)}, \ldots, v_{n_1}^{(1)}; \ldots; v_1^{(r)}, v_2^{(r)}, \ldots, v_{n_r}^{(r)}\right) \to \left(w_1^{(1)}, w_2^{(1)}, \ldots, w_{n_1}^{(1)}; \ldots; w_1^{(r)}, w_2^{(r)}, \ldots, w_{n_r}^{(r)}\right) \tag{9}$$

is given by

$$v = |E(v) - E(w)|, \tag{10}$$

which in a harmonic approximation i.e. when the constants of harmonicity

$$x_{kl}^{(ij)} = 0; \qquad i, j = 1, 2, \ldots, r, \tag{11}$$

is going over into an approximate value

$$v \approx |\left[\pm(v_1^{(1)} - w_1^{(1)})\, v_1^{(1)} \pm \ldots \pm (v_{n_1}^{(1)} - w_{n_1}^{(1)})\, v_{n_1}^{(1)}\right] + \ldots + \\ + \left[\pm(v_1^{(r)} - w_1^{(r)})\, v_1^{(r)} \pm \ldots \pm (v_{n_r}^{(r)} - w_{n_r}^{(r)})\, v_{n_r}^{(r)}\right]|, \tag{12}$$

often used for a symbolic interpretation of the frequency corresponding to the transition (9).

7. In a way entirely analogous to that used for the characterization of the "lower state" by means of the product (7) we can also characterize the "upper state" by means of the product $D(w)$ which differs from $D(v)$ by the change of the quantum number v for w only. Likewise the transformation properties of components of the electric dipole moment P, the magnetic dipole moment μ, and the polarizability tensor α are characterized by irreducible representations of the group $\mathbf{G}$; these representations are usually listed for the group symmetry of lower orders in the character tables of irreducible representations [13], [34], etc.

Thus, if $D(v)$ corresponds to the "lower state" and $D(w)$ to the "upper state" and the representations of components P, μ, α are equal to $\Gamma(P)$, $\Gamma(\mu)$, $\Gamma(\alpha)$, then the spectral line of frequency (10) has a nonzero intensity

a) in the infrared spectrum (because of the change of P) then and only then if $< w \mid P \mid v > \neq 0$. For this value it is necessary and sufficient [10] that

$$D(v) \otimes D(w) \supset \Gamma(P); \tag{13}$$

b) in the infrared spectrum (because of the change of μ) then and only then if $< w \mid \mu \mid v > \neq 0$. For this value it is necessary and sufficient that

$$D(v) \otimes D(w) \supset \Gamma(\mu); \tag{14}$$

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c) in the Raman spectrum (because of the change of α) then and only then if $< w \mid \alpha \mid v > \neq 0$. For this value it is necessary and sufficient that

$$D(v) \otimes D(w) \supset \Gamma(\alpha).$$ (15)

Thus, if the conditions (13), (14), and (15) are fulfilled, we may also say that the spectral line of frequency (10) is infrared or "magnetic" or Raman-active. Considering that the intensity of "magnetic-active" lines has a lower-order value than the intensity of lines given subject to the change of the electric moment, we usually do not regard the "magnetic-active" lines as infrared-active. At the same time it is evident from the three last relations that for the formulation of selection rules it is most important to do both, the splitting (1) and the splitting of the product $D(v) \otimes D(w)$ into the direct sum of irreducible representations of the group $\mathbf{G}$. Now we shall apply the just mentioned rules to a special case i.e. to linear molecules. Here it is convenient to distinguish three cases according to the form of the splitting (1):

1. molecules without a centre of symmetry;
2. molecules with a centre of symmetry having an even number of atoms;
3. molecules with a centre of symmetry having an odd number of atoms.

Let us note that in considering linear molecules a two-way notation is used for irreducible representations as can be seen from the table below (d_i denotes the dimension of irreducible representations).

$\mathbf{C}_{\infty v}$	$A_1 \equiv \Sigma^+$	$A_2 \equiv \Sigma^-$	$E_1 \equiv \Pi$	$E_2 \equiv \Delta$	$E_3 \equiv \Phi$	etc.
$\mathbf{D}_{\infty h}$	$A_{1g} \equiv \Sigma_g^+$ $A_{1u} \equiv \Sigma_u^+$	$A_{2g} \equiv \Sigma_g^-$ $A_{2u} \equiv \Sigma_u^-$	$E_{2g} \equiv \Pi_g$ $E_{1u} \equiv \Pi_u$	$E_{2g} \equiv \Delta_g$ $E_{2u} \equiv \Delta_u$	$E_{3g} \equiv \Phi_g$ $E_{3u} \equiv \Phi_u$	etc.
d_i	1	1	2	2	2	2

3. N-ATOMIC LINEAR MOLECULE OF THE $\mathbf{C}_{\infty v}$ SYMMETRY

This linear molecule does not possess a centre of symmetry. Its atoms carry out $(N - 1)$ normal valence-vibrations i.e. vibrations during which its atoms remain on the same stright line; simple frequencies of the type A_1

$$\nu_1^{(1)}, \nu_1^{(1)}, \ldots, \nu_{N-1}^{(1)},$$

correspond to this case. In addition the molecule carries out $2(N - 2)$ doubly degenerate deformation vibrations having $(N - 2)$ frequencies of the type E_1

$$\nu_1^{(2)}, \nu_2^{(2)}, \ldots, \nu_{N-2}^{(2)},$$

as can be seen from the splitting D_0

$$D_0 = (N - 1) A_1 \oplus (N - 2) E_1,$$ (16)

composed of two types of representations (that means $r = 2$) with dimensions $d_1 = 1, d_2 = 2$. Consequently the term $E(v)$ has the form

$$E(v) = \left[\sum_{k=1}^{N-1} v_k^{(1)}\left(v_k^{(1)} + \frac{1}{2}\right) + \sum_{l=1}^{N-2} v_l^{(2)}(v_l^{(2)} + 1)\right] + \tag{17}$$
$$+ \left[\sum_{k=1}^{N-1} x_k^{(11)}\left(v_k^{(1)} + \frac{1}{2}\right)^2 + \sum_{l=1}^{N-2} x_l^{(22)}(v_l + 1)^2 + \sum_{k=1}^{N-1}\sum_{l=1}^{N-2} x_{kl}^{(12)}\left(v_k^{(1)} + \frac{1}{2}\right)(v_l^{(2)} + 1)\right]$$

and the wave-number v corresponding to the general transition $(v) \to (w)$ equals according to (10) and (17) to the value

$$v \equiv |E(v) - E(w)| = \left[\sum_{k=1}^{N-1} |v_k^{(1)} - w_k^{(1)}| v_k^{(1)} + \sum_{l=1}^{N-2} |v_l^{(2)} - w_l^{(2)}| v_l^{(2)}\right] +$$
$$+ \left[\sum_{k=1}^{N-1} x_k^{(111)} |v_k^{(1)} - w_k^{(1)}| (v_k^{(1)} + w_k^{(1)} + 1) + \sum_{l=1}^{N-2} x_l^{(22)} |v_l^{(2)} - w_l^{(2)}| (v_l^{(2)} + w_l^{(2)} + 2) +$$
$$+ \sum_{k=1}^{N-1}\sum_{l=1}^{N-2} x_{kl}^{(12)}\left|v_k^{(1)} + \frac{1}{2}v_l^{(2)} + v_k^{(1)}v_l^{(2)} - w_k^{(1)} - \frac{1}{2}w_l^{(2)} - w_k^{(1)}w_l^{(2)}\right|\right]. \tag{18}$$

It is possible to draw a general conclusion on the spectral activity of this transition. The expression $D(v)$ as well as the expression $D(w)$ consists of two types of factors

$$D(v) = D_1(v) \otimes D_2(v), \qquad \text{or} \qquad D(w) = D_1(w) \otimes D_2(w), \tag{19}$$

only, whereby

$$D_1(v) = [A_1]^{v_1^{(1)}} \otimes [A_1]^{v_2^{(1)}} \otimes \ldots \otimes [A_1]^{v_{N-1}^{(1)}} = A_1,$$
$$D_2(v) = [E_1]^{v_1^{(2)}} \otimes [E_1]^{v_2^{(2)}} \otimes \ldots \otimes [E_1]^{v_{N-2}^{(2)}}. \tag{20}$$

Since according to [34] it holds

$$[E_1]^{2n} = A_1 \oplus E_2 \oplus E_4 \oplus \ldots \oplus E_{2n}, \tag{21}$$

$$[E_1]^{2n+1} = E_1 \oplus E_3 \oplus E_5 + \ldots + E_{2n+1}, \tag{22}$$

and by definition we put for the arbitrary irreducible representation Γ

$$[\Gamma]^0 = A_1 \qquad \text{or} \qquad [\Gamma]^0 = A_{1g}, \tag{23}$$

it is clear that $D_2(v)$ necessarily contains A_1 or E_1, for if all numbers $v_i^{(2)}$ are even then each of symmetrical powers contains $[E_1]^{v_i^{(2)}} \supset A_1$. If $v_i^{(2)}$ are odd numbers, then the product of identical representations will necessarily appear in $D(v)$ and thus also the product

$$E_1 \otimes E_1 = A_1 \oplus A_2 \oplus E_2.$$

If finally the numbers $v_i^{(2)}$ have a different parity, the product $A_1 \otimes E_1 = E_1$ will appear in $D_2(v)$. Entirely analogous consideration can be constructed for $D(v) \otimes D(w)$; lastly we arrive to a conclusion which leads us to

$$D(v) \otimes D(w) = D_1(v) \otimes D_1(w) \otimes D_2(v) \otimes D_2(w) \supset A_1 \vee E_1.$$

Considering that according to A_1 and E_1 the components of the moments are transformed, i.e.

$$A_1\{P_z; \alpha_{xx} + \alpha_{yy}, \alpha_{zz}\}, \quad E_1\{(P_x; P_y); \ (\mu_x, \mu_y); \ (\alpha_{yz}, \alpha_{zx})\}, \tag{25}$$

it follows from (24), (13), and (15) that the general combination frequency (18) is both infrared $-$, and Raman-active. Thus, all the conceivable frequencies i.e. fundamental, difference, and combination frequencies for all linear molecules without a centre of symmetry are both infrared and Raman-active.

Thus in measuring various frequencies v by the spectroscopic method, we can according to (18) compute constants of anharmonicity $x_k^{(11)}$, $x_l^{(22)}$, $x_{kl}^{(12)}$ wherein $k = 1, 2, \ldots, N - 1, l = 1, 2, \ldots, N - 2$. Of particular importance to us are the special cases:

a) A special case of combination frequencies (18) are difference frequencies characterized by the nonzero value of merely two homothetic numbers in either term of (18), e.g. of numbers $v_n^{(1)}$, $w_n^{(1)}$ or $v_m^{(2)}$, $w_m^{(2)}$; all the other quantum numbers are zero so that the frequencies of difference lines are equal to

$$''v_n^{(1)}v_n^{(1)} - w_n^{(1)}v_n^{(1)''} = \tag{26}$$
$$= |\, v_n^{(1)} - w_n^{(1)}\,|\, v_n^{(1)} + \{x_n^{(11)}\,|\,(v_n^{(1)} - w_n^{(1)})(v_n^{(1)} + w_n^{(1)} + 1)\,| + x_{nl}^{(12)}\,|\, v_n^{(1)} - w_n^{(1)}\,|\},$$

$$''v_m^{(2)}v_m^{(2)} - w_m^{(2)}v_m^{(2)''} = |\, v_m^{(2)} - w_m^{(2)}\,|\, v_m^{(2)} +$$
$$+ \left\{x_m^{(22)}\,|\,(v_m^{(2)} - w_m^{(2)})(v_m^{(2)} + w_m^{(2)} + 2)\,| + \frac{1}{2} x_{km}^{(12)}\,|\, v_m^{(2)} - w_m^{(2)}\,|\right\}, \tag{27}$$

$$n = 1, 2, \ldots, N - 1; \qquad m = 1, 2, \ldots N - 2.$$

The symbols for frequencies of spectral lines derived from a harmonic approximation are labelled with quotation marks.

b) A special case of difference frequencies are harmonic frequencies where only one quantum number is in one term different from zero, i.e. one of numbers $v_n^{(1)} \ne 0$ or $v_m^{(2)} \ne 0$. Consequently from (26) and (27) it follows for harmonic frequencies

$$''v_n^{(1)}v_n^{(1)''} = v_n^{(1)}v_n^{(1)} + [x_n^{(11)} \cdot v_n^{(1)}(v_n^{(1)} + 1) + x_{nl}^{(12)} \cdot v_n^{(1)}], \tag{28}$$

$$''v_m^{(2)}v_m^{(2)''} = v_m^{(2)}v_m^{(2)} + \left[x_m^{(22)} \cdot v_m^{(2)}(v_m^{(2)} + 2) + \frac{1}{2} x_{km}^{(12)} \cdot v_m^{(2)}\right]. \tag{29}$$

c) A special case of harmonic frequencies are fundamental frequencies to which belong $v_n^{(1)} = 1$ or $v_m^{(2)} = 1$. From (28) and (29) it results

$$''v_n^{(1)''} = v_n^{(1)} + (2x_n^{(11)} + x_{nl}^{(12)}), \tag{30}$$

$$''v_m^{(2)''} = v_m^{(2)} + \left(3x_m^{(22)} + \frac{1}{2} x_{km}^{(12)}\right). \tag{31}$$

The simplest cases of the mentioned type of molecules are XY molecules for which $D_0 = A_1$ so that the term and the frequency of transition $(v) \to (w)$ equal to

$$E(v) = v\left(v + \frac{1}{2}\right) + x\left(v + \frac{1}{2}\right)^2, \tag{32}$$

$$v \equiv \mid E(v) - E(w) \mid = [v + x(v + w + 1)] \cdot \mid v - w \mid. \tag{33}$$

Hence fundamental or harmonic or difference frequencies are equal to

$$''v'' = v + 2x, \tag{34}$$

$$''vv'' = vv + xv(v + 1), \tag{35}$$

$$''vv - wv'' = [v + x(v + w + 1)] \cdot \mid v - w \mid. \tag{36}$$

For molecules XYZ there holds $D = 2A \oplus E_1$ so that

$$E(v_1^{(1)}, v_2^{(1)}; v_1^{(2)}) = \left[v_1^{(1)}\left(v_1^{(1)} + \frac{1}{2}\right) + v_2^{(1)}\left(v_2^{(1)} + \frac{1}{2}\right) + v_1^{(2)}(v_1^{(2)} + 1) \right] +$$
$$+ \left[x_1^{(11)}\left(v_1^{(1)} + \frac{1}{2}\right)^2 + x_2^{(11)}\left(v_2^{(1)} + \frac{1}{2}\right)^2 + x_1^{(22)}(v_1^{(2)} + 1)^2 + \right.$$
$$+ x_{12}^{(11)}\left(v_1^{(1)} + \frac{1}{2}\right)\left(v_2^{(1)} + \frac{1}{2}\right) + x_{11}^{(12)}\left(v_1^{(1)} + \frac{1}{2}\right)(v_1^{(2)} + 1) +$$
$$\left. + x_{21}^{(12)}\left(v_2^{(1)} + \frac{1}{2}\right)(v_1^{(2)} + 1) \right] \tag{37}$$

and fundamental frequencies are equal to

$$''v_1^{(1)}'' = v_1^{(1)} + \left(2x_1^{(11)} + \frac{1}{2}x_{12}^{(11)} + x_{11}^{(12)}\right), \tag{38}$$

$$''v_2^{(1)}'' = v_2^{(1)} + \left(2x_2^{(11)} + \frac{1}{2}x_{12}^{(11)} + x_{21}^{(12)}\right), \tag{39}$$

$$''v_1^{(2)}'' = v_1^{(2)} + \left(3x_1^{(22)} + \frac{1}{2}x_{11}^{(12)} + x_{21}^{(12)}\right), \tag{40}$$

harmonic frequencies are equal to

$$''v_1^{(1)}v_1^{(1)}'' = v_1^{(1)}v_1^{(1)} + \left[x_1^{(11)}(v_1^{(1)} + 1)\,v_1^{(1)} + \frac{1}{2}x_{12}^{(11)}v_1^{(1)} + x_{11}^{(12)}v_1^{(1)} \right], \tag{41}$$

$$''v_2^{(1)}v_2^{(1)}'' = v_2^{(1)}v_2^{(1)} + \left[x_2^{(11)}(v_2^{(1)} + 1)\,v_2^{(1)} + \frac{1}{2}x_{12}^{(11)}v_2^{(1)} + x_{21}^{(12)}v_2^{(1)} \right], \tag{42}$$

$$''v_1^{(2)}v_1^{(2)}'' = v_1^{(2)}v_1^{(2)} + \left[x_1^{(22)}(v_1^{(2)} + 2)\,v_1^{(2)} + \frac{1}{2}x_{11}^{(12)}v_1^{(2)} + \frac{1}{2}x_{21}^{(12)}v_1^{(2)} \right], \tag{43}$$

difference frequencies are equal to

$$''v_1^{(1)}v_1^{(1)} - w_1^{(1)}v_1^{(1)}'' = \mid v_1^{(1)} - w_1^{(1)} \mid v_1^{(1)} + \left\{ x_1^{(11)}(v_1^{(1)} + w_1^{(1)} + 1) \cdot \mid v_1^{(1)} - w_1^{(1)} \mid + \right.$$
$$\left. + \frac{1}{2}x_{12}^{(11)} \cdot \mid v_1^{(1)} - w_1^{(1)} \mid + x_{11}^{(12)} \cdot \mid v_1^{(1)} - w_1^{(1)} \mid \right\}, \tag{44}$$

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$$''v_2^{(1)}v_2^{(1)} - w_2^{(1)}v_2^{(1)''} = |v_2^{(1)} - w_2^{(1)}|v_2^{(1)} + \left\{ x_2^{(11)}(v_2^{(1)} + w_2^{(1)} + 1) \cdot |v_2^{(1)} - w_2^{(1)}| + \right.$$

$$\left. + \frac{1}{2} x_{12}^{(11)} \cdot |v_2^{(1)} - w_2^{(1)}| + x_{21}^{(12)} \cdot |v_2^{(1)} - w_2^{(1)}| \right\}, \tag{45}$$

$$''v_1^{(2)}v_1^{(2)} - w_1^{(2)}v_1^{(2)''} = |v_1^{(2)} - w_1^{(2)}|v_1^{(2)} + \left\{ x_1^{(22)}(v_1^{(2)} + w_1^{(2)} + 2) \cdot |v_1^{(2)} - w_1^{(2)}| + \right.$$

$$\left. + \frac{1}{2} x_{11}^{(12)} \cdot |v_1^{(2)} - w_1^{(2)}| + \frac{1}{2} x_{21}^{(12)} \cdot |v_1^{(2)} - w_1^{(2)}| \right\} \tag{46}$$

and combination frequencies are equal to

$$''v_1^{(1)}v_1^{(1)} + v_2^{(1)}v_2^{(1)} + v_1^{(2)}v_1^{(2)} - w_1^{(1)}v_1^{(1)} - w_2^{(1)}v_2^{(1)} - w_1^{(2)}v_1^{(2)''} \equiv |E(v) - E(w)| =$$

$$= \{|v_1^{(1)} - w_1^{(1)}|v_1^{(1)} + |v_2^{(1)} - w_2^{(1)}|v_2^{(1)} + |v_1^{(2)} - w_1^{(2)}|v_1^{(2)}\} +$$

$$+ \left\{ x_1^{(11)} \cdot (v_1^{(1)} + w_1^{(1)} + 1) \cdot |v_1^{(1)} - w_1^{(1)}| + x_2^{(11)} \cdot (v_2^{(1)} + w_2^{(1)} + 1) \cdot |v_2^{(1)} - w_2^{(1)}| + \right.$$

$$+ x_1^{(22)} \cdot (v_1^{(2)} + w_1^{(2)} + 2) \cdot |v_1^{(2)} - w_1^{(2)}| +$$

$$+ x_{12}^{(11)} \cdot \left| v_1^{(1)}v_2^{(1)} - w_1^{(1)}w_2^{(1)} + \frac{1}{2} v_1^{(1)} - \frac{1}{2} w_1^{(1)} + \frac{1}{2} v_2^{(1)} - \frac{1}{2} w_2^{(1)} \right| +$$

$$+ x_{11}^{(12)} \cdot \left| v_1^{(1)}v_1^{(2)} - w_1^{(1)}w_1^{(2)} + v_1^{(1)} - w_1^{(1)} + \frac{1}{2} v_1^{(2)} - \frac{1}{2} w_1^{(2)} \right| +$$

$$+ \left. x_{21}^{(12)} \left| v_2^{(1)}v_1^{(2)} - w_2^{(1)}w_1^{(2)} + v_2^{(1)} - w_2^{(1)} + \frac{1}{2} v_1^{(2)} - \frac{1}{2} w_1^{(2)} \right| \right\}. \tag{47}$$

4. 2p-ATOMIC LINEAR MOLECULE OF $\mathbf{D}_{\infty h}$ SYMMETRY

The decay D_0 has the form

$$D_0 = pA_{1g} \oplus (p - 1)(A_{1u} \oplus E_{1g} \oplus E_{1u}), \tag{48}$$

Consequently the molecule carries out $6p - 5$ normal oscillations with $4p - 3$ different fundamental frequencies

$$''v_k^{(1)}(A_{1g})''; \quad k = 1, 2, \dots p, \tag{49}$$

$$''v_l^{(2)}(A_{1u})'', \quad ''v_l^{(3)}(E_{1g})'', \quad ''v_l^{(4)}(E_{1u})''; \quad l = 1, 2, \dots, p - 1.$$

According to [34] holds

$$A_{1g}\{\alpha_{xx} + \alpha_{yy}, \alpha_{zz}\}, \qquad A_{1u}\{P_s\}, \tag{51}$$

$$E_{1g}\{(\mu_x, \mu_y)_1 (\alpha_{yz}, \alpha_{zz})\}, \qquad E_{1u}\{(P_x, P_y)\}, \tag{52}$$

and it is clear that all of the mentioned frequencies having in their irreducible representation index u are infrared active and all those with index g are Raman-active. Comparison of D_0 in (16) with that given in (48) shows that in both cases D_0 contains only representations A_1 and E_1, so that with analogous considerations as in the

previous paragraph we could arrive at a conclusion (24). The only difference between these two cases is made by the indices g and u with respect to molecules of symmetry $\mathbf{D}_{\infty h}$; in determinating the presence of index g or u in the product (24) it is possible to use the rules for the multiplication of irreducible representations [34]

$$g \times g = u \times u = g, \tag{53}$$

$$g \times u = u, \tag{54}$$

and for symmetrical powers of irreducible representations [34]

$$[g]^{2n} = [u]^{2n} = g, \tag{55}$$

$$[g]^{2n+1} = [u]^{2n+1} = u, \tag{56}$$

and also according to (23).

Thus the product $D(v) \times D(w)$ has the form

$$\prod_{k=1}^{p} [A_{1g}]^{v_k^{(1)}} \otimes [A_{1g}]^{w_k^{(1)}} \otimes \prod_{l=1}^{p-1} [A_{1u}]^{v_l^{(2)}} [A_{1u}]^{w_l^{(2)}} \otimes [E_{1g}]^{v_l^{(3)}} \otimes [E_{1g}]^{w_l^{(3)}} \otimes [E_{1u}]^{v_l^{(4)}} \otimes$$
$$\otimes [E_{1u}]^{w_l^{(4)}} \tag{57}$$

and it is to determine in which cases the expression

$$D(v) \otimes D(w) \supset A_{1g} \vee E_{1g} \Rightarrow \langle v \mid \alpha \mid w \rangle \neq 0, \tag{58}$$

and in which cases that of

$$D(v) \otimes D(w) \supset A_{1u} \vee E_{1u} \Rightarrow \langle v \mid P \mid w \rangle \neq 0, \tag{59}$$

hold. First, let us decide in which cases the condition (59) is satisfied. It is clear, due to (54) that in the product (57) a representation with index u i.e. Γ_u is contained, if the total number of factors with respect to type $[\Gamma]^v$ containing Γ_u is an odd number. Thereby the factors $[\Gamma]^v$ contain Γ_u when $[\Gamma_u]^{2n-1}$ and when $[\Gamma_g]^{2n+1}$ thus not when $[\Gamma_g]^1$; $n = 1, 2, 3, \ldots$. It is possible to conclude that the condition (59) is satisfied and the frequency is infrared active if the total number of quantum numbers assuming odd values in

$$v_k^{(1)} > 1, \qquad w_k^{(1)} > 1, \qquad v_l^{(3)} > 1, \qquad w_l^{(3)} > 1; \qquad v_l^{(2)} > 0, \qquad w_l^{(2)} > 0,$$
$$v_l^{(4)} > 0, \qquad w_l^{(4)} > 0, \tag{60}$$
$$(k = 1, 2, \ldots, p; \qquad l = 1, 2, \ldots, p-1),$$

is an odd number. In all other cases is the condition (58) satisfied i.e. the frequencies are Raman-active.

The term $E(v)$ has the form

$$E(v) = \left\{ \sum_{k=1}^{p} v_k^{(1)} \left(v_k^{(1)} + \frac{1}{2} \right) + \sum_{l=1}^{p-1} \left[v_l^{(2)} \left(v_l^{(2)} + \frac{1}{2} \right) + v_l^{(3)}(v_l^{(3)} + 1) + v_l^{(4)}(v_l^{(4)} + 1) \right] \right\} +$$
$$+ \left\{ \sum_{k=1}^{p} x_k^{(11)} \left(v_k^{(1)} + \frac{1}{2} \right)^2 + \sum_{l=1}^{p-1} \left[x_l^{(22)} \left(v_l^{(2)} + \frac{1}{2} \right)^2 + x_l^{(33)}(v_l^{(3)} + 1)^2 + x_l^{(44)}(v_l^{(4)} + 1)^2 \right] \right\} +$$

$$+ \sum_{k=1}^{p} \sum_{l=1}^{p-1} \left[x_{kl}^{(12)} \left(v_k^{(1)} + \frac{1}{2} \right) \left(v_l^{(2)} + \frac{1}{2} \right) + x_{kl}^{(13)} \left(v_k^{(1)} + \frac{1}{2} \right) (v_l^{(3)} + 1) + \right.$$

$$+ x_{kl}^{(14)} \left(v_k^{(1)} + \frac{1}{2} \right)(v_l^{(4)} + 1) + x_{kl}^{(23)} \left(v_k^{(2)} + \frac{1}{2} \right)(v_l^{(3)} + 1) + x_{kl}^{(24)} \left(v_k^{(2)} + \frac{1}{2} \right) \times$$

$$\left. \times (v_l^{(4)} + 1) + x_{kl}^{(34)} (v_k^{(3)} + 1)(v_l^{(4)} + 1) \right] \Bigg\} . \tag{61}$$

From the above it is now easy to derive formulas for:

a) combination frequencies

$$v \equiv | E(v) - E(w) | = \{ \sum_{k=1}^{p} v_k^{(1)} . | v_k^{(1)} - w_k^{(1)} | +$$

$$+ \sum_{l=1}^{p-1} \left[v_l^{(2)} . | v_l^{(2)} - w_l^{(2)} | + v_l^{(3)} . | v_l^{(3)} - w_l^{(3)} | + v_l^{(4)} . | v_l^{(4)} - w_l^{(4)} | \right] \} +$$

$$+ \{ \sum_{k=1}^{p} x_k^{(11)} . | v_k^{(1)} - w_k^{(1)} | . (v_k^{(1)} + w_k^{(1)} + 1) +$$

$$+ \sum_{l=1}^{p-1} \left[x_l^{(22)} . | v_l^{(2)} - w_l^{(2)} | . (v_l^{(2)} + w_l^{(2)} + 1) + x_l^{(33)} | v_l^{(3)} - w_l^{(3)} | . (v_l^{(3)} + w_l^{(3)} + 2) + \right.$$

$$\left. + x_l^{(44)} . | v_l^{(4)} - w_l^{(4)} | . (v_l^{(4)} + w_l^{(4)} + 2) \right] +$$

$$+ \sum_{k=1}^{p} \sum_{l=1}^{p-1} \left[x_{kl}^{(12)} . \left| v_k^{(1)} v_l^{(2)} - w_k^{(1)} w_l^{(2)} + \frac{1}{2} (v_k^{(1)} - w_k^{(1)}) + \frac{1}{2} (v_l^{(2)} - w_l^{(2)}) \right| + \right.$$

$$+ x_{kl}^{(13)} . \left| v_k^{(1)} v_l^{(3)} - w_k^{(1)} w_l^{(3)} + (v_k^{(1)} - w_k^{(1)}) + \frac{1}{2} (v_l^{(3)} - w_l^{(3)}) \right| +$$

$$+ x_{kl}^{(14)} . \left| v_k^{(1)} v_l^{(4)} - w_k^{(1)} w_l^{(4)} + (v_k^{(1)} - w_k^{(1)}) + \frac{1}{2} (v_l^{(4)} - w_l^{(4)}) \right| +$$

$$+ x_{kl}^{(23)} . \left| v_k^{(2)} v_l^{(3)} - w_k^{(2)} w_l^{(3)} + (v_k^{(2)} - w_k^{(2)}) + \frac{1}{2} (v_l^{(3)} - w_l^{(3)}) \right| +$$

$$+ x_{kl}^{(24)} . \left| v_k^{(2)} v_l^{(4)} - w_k^{(2)} w_l^{(4)} + (v_k^{(2)} - w_k^{(2)}) + \frac{1}{2} (v_l^{(4)} - w_l^{(4)}) \right| +$$

$$\left. + x_{kl}^{(34)} . | v_k^{(3)} v_l^{(4)} - w_k^{(3)} w_l^{(4)} + (v_k^{(3)} - w_k^{(3)}) + (v_l^{(4)} - w_l^{(4)}) | \right] \Bigg\} ; \tag{62}$$

b) difference frequencies which are $\genfrac{}{}{0pt}{}{\text{infrared}}{\text{Raman-active}}$ if the quantum numbers have $\genfrac{}{}{0pt}{}{\text{the opposite}}{\text{the same}}$ parity:

$${}^{\prime\prime} v_k^{(1)} v_k^{(1)} - w_k^{(1)} v_k^{(1)} {}^{\prime\prime} = v_k^{(1)} . | v_k^{(1)} - w_k^{(1)} | + x_k^{(11)} . | v_k^{(1)} - w_k^{(1)} | . (v_k^{(1)} + w_k^{(1)} + 1) +$$

$$+ \frac{1}{2} x_{kl}^{(12)} . | v_k^{(1)} - w_k^{(1)} | + x_{kl}^{(13)} . | v_k^{(1)} - w_k^{(1)} | + x_{kl}^{(14)} . | v_k^{(1)} - w_k^{(1)} | , \tag{63}$$

$${}^{\prime\prime} v_l^{(2)} v_l^{(2)} - w_l^{(2)} v_l^{(2)} {}^{\prime\prime} = v_l^{(2)} . | v_l^{(2)} - w_l^{(2)} | + x_l^{(22)} . | v_l^{(2)} - w_l^{(2)} | . (v_l^{(2)} + w_l^{(2)} + 1) +$$

$$+ \frac{1}{2} x_{kl}^{(12)} . | v_l^{(2)} - w_l^{(2)} | + x_{kl}^{(23)} . | v_k^{(2)} - w_k^{(2)} | + x_{kl}^{(24)} . | v_k^{(2)} - w_k^{(2)} | , \tag{64}$$

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$$''v_l^{(3)} v_l^{(3)} - w_l^{(3)} v_l^{(3)''} = v_l^{(3)} . |v_l^{(3)} - w_l^{(3)}| + x_l^{(33)} . |v_l^{(3)} - w_l^{(3)}| . (v_l^{(3)} + w_l^{(3)} + 2) +$$

$$+ \frac{1}{2} x_{kl}^{(13)} |v_l^{(3)} - w_l^{(3)}| + \frac{1}{2} x_{kl}^{(23)} . |v_l^{(3)} - w_l^{(3)}| + x_{kl}^{(34)} . |v_k^{(3)} - w_k^{(3)}|, \quad (65)$$

$$''v_l^{(4)} v_l^{(4)} - w_l^{(4)} v_l^{(4)''} = v_l^{(4)} . |v_l^{(4)} - w_l^{(4)}| + x_l^{(44)} . |v_l^{(4)} - w_l^{(4)}| . (v_l^{(4)} + w_l^{(4)} + 2) +$$

$$+ \frac{1}{2} x_{kl}^{(14)} . |v_l^{(4)} - w_l^{(4)}| + \frac{1}{2} x_{kl}^{(24)} . |v_l^{(4)} - w_l^{(4)}| + x_{kl}^{(34)} . |v_l^{(4)} - w_l^{(4)}|, \quad (66)$$

c) harmonic frequencies (which are Raman-active for $v_k^{(i)} = 2n$ and infrared-active for $v_k^{(i)} = 2n + 1$, $i = 1, 2, 3, 4$)

$$''v_k^{(1)} v_k^{(1)''} = v_k^{(1)} v_k^{(1)} + x_l^{(11)} . v_k^{(1)}(v_k^{(1)} + 1) + \frac{1}{2} x_{kl}^{(12)} v_l^{(1)} + x_{kl}^{(13)} v_l^{(1)} + x_{kl}^{(14)} v_l^{(1)}, (67)$$

$$''v_l^{(2)} v_l^{(2)''} = v_l^{(2)} v_l^{(2)} + x_l^{(22)} . v_l^{(2)}(v_l^{(2)} + 1) + \frac{1}{2} x_{kl}^{(12)} v_l^{(2)} + x_{kl}^{(23)} v_k^{(2)} + x_{kl}^{(24)} v_k^{(2)}, (68)$$

$$''v_l^{(3)} v_l^{(3)''} = v_l^{(3)} v_l^{(3)} + x_l^{(33)} v_l^{(3)}(v_l^{(3)} + 2) + \frac{1}{2} x_{kl}^{(13)} v_l^{(3)} + \frac{1}{2} x_{kl}^{(23)} v_l^{(3)} + x_{kl}^{(34)} v_k^{(3)}, (69)$$

$$''v_l^{(4)} v_l^{(4)''} = v_l^{(4)} v_l^{(4)} + x_l^{(44)} v_l^{(4)}(v_l^{(4)} + 2) + \frac{1}{2} x_{kl}^{(14)} v_l^{(4)} + \frac{1}{2} x_{kl}^{(24)} v_l^{(4)} + x_{kl}^{(34)} v_l^{(4)}, (70)$$

and

d) fundamental frequencies

$$''v_k^{(1)''} = v_k^{(1)} + 2x_k^{(11)} + \frac{1}{2} x_{kl}^{(12)} + x_{kl}^{(13)} + x_{kl}^{(14)}, \tag{71}$$

$$''v_l^{(2)''} = v_l^{(2)} + 2x_l^{(22)} + \frac{1}{2} x_{kl}^{(12)} + x_{kl}^{(23)} + x_{kl}^{(24)}, \tag{72}$$

$$''v_l^{(3)''} = v_l^{(3)} + 3x_l^{(33)} + \frac{1}{2} x_{kl}^{(13)} + \frac{1}{2} x_{kl}^{(23)} + x_{kl}^{(34)}, \tag{73}$$

$$''v_l^{(4)''} = v_l^{(4)} + 3x_l^{(44)} + \frac{1}{2} x_{kl}^{(14)} + \frac{1}{2} x_{kl}^{(24)} + x_{kl}^{(34)}, \tag{74}$$

Frequencies $''v_l^{(2)''}$ and $''v_l^{(4)''}$ are infrared-active, frequencies $''v_k^{(1)''}$ and $''v_l^{(3)''}$ are Raman active.

The simplest case of the above mentioned molecules are the X_2 molecules for which $D_0 = A_{1g}$, i.e. the term and the frequency of transition $(v) \to (w)$ are identical with analogous expressions (32) through (36). The fundamental frequency is Raman-active. Infrared active are odd harmonics only, and from the difference frequencies but those, for which the numbers v, w are of the opposite parity. These facts explain the high transparency for the infrared radiation of the earth atmosphere which is predominantly formed by diatomic gases.

5. $(2p + 1)$-ATOMIC LINEAR MOLECULE OF SYMMETRY $\mathbf{D}_{\infty h}$

From the splitting

$$\mathbf{D}_0 = p(A_{1g} \oplus A_{1u} \oplus E_{1u}) \oplus (p - 1) E_{1g}, \tag{75}$$

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results that the molecule carries out $(6p - 2)$ normal oscillations with $(4p - 1)$ fundamental frequencies. Since the same group of symmetry as in paragraph 4 is concerned and the splitting (75) differs from (48) only by the number of irreducible representations in D_0, it is apparent that the same selection rules are true. The frequencies of spectral lines are given by expressions analogous to those in (62) through (74). Consequently the most convenient way is to change in all expressions of paragraph 4 a) the wave numbers

$$v_k^{(1)}(A_{1g}) \to v_k^{(1)}(A_{1g}), \ v_l^{(2)}(A_{1u}) \to v_k^{(2)}(A_{1u}), \ v_l^{(3)}(E_{1g}) \to v_l^{(3)}(E_{1g}),$$
$$v_l^{(4)}(E_{1u}) \to v_k^{(4)}(E_{1u}), \tag{76}$$

b) quantum numbers

$$v_k^{(1)}, \ w_k^{(1)} \to v_k^{(1)}, \ w_k^{(1)}; \ v_l^{(2)}, \ w_l^{(2)} \to v_k^{(2)}, \ w_k^{(2)}; \ v_l^{(3)}, \ w_l^{(3)} \to v_l^{(3)}, \ w_l^{(3)};$$
$$v_l^{(4)}, \ w_l^{(4)} \to v_k^{(4)}, \ w_k^{(4)} \tag{77}$$

and c) the summation signs—whereby $k = 1, 2, \ldots, p$; $l = 1, 2, \ldots, p - 1$. Therefore the analogous expressions will not be introduced explicitly and our study will be restricted to the simplest case, i.e. to molecules of the type X_3 and YXY.

For both molecules holds

$$\mathbf{D}_0 = A_{1g} \oplus A_{1u} \oplus E_{1u}, \tag{78}$$

i.e. in both cases are the combination frequencies equal to

$$"v" = v^{(1)}. \, | \, v^{(1)} - w^{(1)} \, | + v^{(2)}. \, | \, v^{(2)} - w^{(2)} \, | + v^{(3)}. \, | \, v^{(3)} - w^{(3)} \, | +$$
$$+ \, x^{(11)}. \, | \, v^{(1)} - w^{(1)} \, | . \, (v^{(1)} + w^{(1)} + 1) +$$
$$+ \, x^{(12)}. \, \left| \, v^{(1)} v^{(2)} - w^{(1)} w^{(2)} + \frac{1}{2} (v^{(1)} - w^{(1)}) + \frac{1}{2} (v^{(2)} - w^{(2)}) \right| +$$
$$+ \, x^{(13)}. \, \left| \, v^{(1)} v^{(3)} - w^{(1} \, w^{(3)} + (v^{(1)} - w^{(1)}) + \frac{1}{2} (v^{(3)} - w^{(3)}) \right| +$$
$$+ \, x^{(22}. \, | \, v^{(2)} - w^{(2)} \, | . \, (v^{(2)} + w^{(2)} + 1) +$$
$$+ \, x^{(23)}. \, \left| \, v^{(2)} v^{(3)} - w^{(2)} w^{(3)} + (v^{(2)} - w^{(2)}) + \frac{1}{2} (v^{(3)} - w^{(3)}) \right| +$$
$$+ \, x^{(33)}. \, | \, v^{(3)} - w^{(3)} \, | . \, (v^{(3)} + w^{(3)} + 2); \tag{79}$$

(The lower index 1 being for all members the same, is omitted). Difference frequencies

$$"v^{(1)} v^{(1)} - w^{(1)} v^{(1)}" = v^{(1)} \, | \, v^{(1)} - w^{(1)} \, | + x^{(11)}. \, | \, v^{(1)} - w^{(1)} \, | . \, (v^{(1)} + w^{(1)} + 1) +$$
$$+ \frac{1}{2} x^{(12)}. \, | \, v^{(1)} - w^{(1)} \, | + x^{(13)} \, | \, v^{(1)} - w^{(1)} \, |, \tag{80}$$

are infrared active if one of the numbers $v^{(1)}$, $w^{(1)}$ is odd and larger than two. In other cases are the frequencies Raman-active.

$$''v^{(2)}v^{(2)} - w^{(2)}v^{(2)''} = v^{(2)}.\,|\,v^{(2)} - w^{(2)}\,| + \frac{1}{2}x^{(12)}.\,|\,v^{(2)} - w^{(2)}\,| +$$
$$+ x^{(22)}.\,|\,v^{(2)} - w^{(2)}\,|\,.\,(v^{(2)} + w^{(2)} + 1) + x^{(23)}.\,|\,v^{(2)} - w^{(2)}\,|, \tag{81}$$

$$''v^{(3)}v^{(3)} - w^{(3)}v^{(3)''} = v^{(3)}.\,|\,v^{(3)} - w^{(3)}\,| + \frac{1}{2}x^{(13)}.\,|\,v^{(3)} - w^{(3)}\,| +$$
$$+ \frac{1}{2}x^{(23)}.\,|\,v^{(3)} - w^{(3)}\,| + x^{(33)}.\,|\,v^{(3)} - w^{(3)}\,|\,.\,(v^{(3)} + w^{(3)} + 2). \tag{82}$$

Harmonic frequencies

$$''v^{(1)}v^{(1)''} = v^{(1)}v^{(1)} + x^{(11)}v^{(1)}(v^{(1)} + 1) + \frac{1}{2}x^{(12)}v^{(1)} + x^{(13)}v^{(1)}, \tag{83}$$

$$''v^{(2)}v^{(2)''} = v^{(2)}v^{(2)} + \frac{1}{2}x^{(12)}v^{(2)} + x^{(22)}.\,v^{(2)}(v^{(2)} + 1) + x^{(23)}v^{(2)}, \tag{84}$$

$$''v^{(3)}v^{(3)''} = v^{(3)}v^{(3)} + \frac{1}{2}x^{(13)}v^{(3)} + \frac{1}{2}x^{(23)}v^{(3)} + x^{(33)}v^{(3)}(v^{(3)} + 2), \tag{85}$$

are infrared active if the quantum numbers $v^{(i)} \geqq 3$ are odd — in the contrary case Raman-active frequencies are in question.
From fundamental frequencies

$$''v^{(1)''} = v^{(1)} + 2x^{(11)} + \frac{1}{2}x^{(12)} + x^{(13)}, \tag{86}$$

$$''v^{(2)''} = v^{(2)} + \frac{1}{2}x^{(12)} + 2x^{(22)} + x^{(23)}, \tag{87}$$

$$''v^{(3)''} = v^{(3)} + \frac{1}{2}x^{(13)} + \frac{1}{2}x^{(23)} + 3x^{(33)}, \tag{88}$$

only (86) is Raman-active while the other frequencies are infrared active.

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Shrnutí

VIBRAČNÍ ENERGIE LINEÁRNÍCH MOLEKUL A DOVOLENÉ PŘECHODY V INFRAČERVENÉM A RAMANOVĚ SPEKTRU

VLADIMÍR MALÍŠEK

V odstavci prvém jsou naznačeny možnosti praktických aplikací teorie grup ve spektroskopii lineárních molekul. V odstavci druhém jsou obecně formulovány vztahy mezi kvantově-mechanickými a grupově-teoretickými charakteristikami vibračního stavu obecné N-atomové molekuly, jež spočívají v tomto: rozloží-li se „vibrační representace molekuly" D_0 v direktní součet r ireducibilních representací (1),

v nichž index d_i udává rozměr ireducibilní representace $\Gamma_{d_i}^{(i)}$, je vlastní hodnota vibrační energie molekuly (5), stejně jako vlastní vektor (6), funkcí vibračních kvantových čísel a vlastnosti symetrie charakterisuje součin r symetrických mocnin ireducibilních representací (7), (8). Vlnočet odpovídající přechodu (9) je dán výrazem (10), případně v aproximaci N-bodového harmonického oscilátoru výrazem (12) a je infračerveně, resp. ramanovsky aktivní, jestliže je splněna podmínka (13), resp. (15).

V dalších odstavcích se studují popsaným postupem lineární N-atomové molekuly, jež se podle tvaru D_0 rozdělují do tří skupin:

a) molekuly bez středu symetrie ($\mathbf{C}_{\infty v}$), odstavec 3.,

b) molekuly se středem symetrie ($\mathbf{D}_{\infty h}$) se sudým počtem atomů, odstavec 4.,

c) molekuly se středem symetrie ($\mathbf{D}_{\infty h}$) s lichým počtem atomů, odstavec 5.

V případě *a)* udává rozklad D_0 vztah (16); kombinační frekvence (18), diferenční (26) a (27), harmonické (28) a (29) a fundamentální (30) a (31). Přitom všechny myslitelné frekvence u molekul symetrie $\mathbf{C}_{\infty v}$ jsou jak infračerveně, tak ramanovsky aktivní. Nejdůležitějším příkladem molekul tohoto typu je molekula XY, jejíž frekvence popisují relace (32) až (36) a molekula XYZ, pro niž platí (37) až (46).

V případě *b)* má D_0 tvar (48), term (61), frekvence kombinační (62), diferenční (63) až (66), harmonické (67) až (70) a fundamentální (71) až (74). Příkladem je molekula X_2, pro jejíž frekvence platí relace shodné s (32) až (36). Výběrové pravidlo lze formulovat tak, že frekvence jsou infračerveně, resp. ramanovsky aktivní, jestliže celkový počet kvantových čísel nabývajících lichých hodnot a splňujících podmínku (60), je lichý.

V případě *c)* má $\mathbf{D}_0$ tvar (75), jenž se liší od obdobného výrazu v případě *b)* pouze koeficienty udávajícími počet ireducibilních representací v $\mathbf{D}_0$, takže platí stejné výběrové pravidlo jako v případě *b)*. Rovněž frekvence spektrálních čar jsou dány výrazy (62) až (74), v nichž stačí provést záměnu v označení vlnočtů podle (76) a kvantových čísel podle (77). Nejjednodušším příkladem v této skupině jsou molekuly X_3 a YXY symetrie $\mathbf{D}_{\infty h}$, pro něž platí stejné vzorce, a to vztah (79) pro frekvence kombinační, (80) až (82) pro diferenční, (83) až (85) pro harmonické a (86) až (88) pro frekvence fundamentální.