SYMMETRY CONCEPT APPLIED IN MOLECULAR SPECTROSCOPY

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Abstract

This paper deals with establishment of the permitted transitions in the rotational spectra of a molecule belonging to commutative point group C_{2v} *and having the two-fold axis parallel to the main axis corresponding to the smallest value of the inertia moment (*$O-CH_2$*- formaldehyde). The molecule is considered as being a rigid top in this study.*

Keywords: *point groups of low symmetry, formaldehyde, pure rotation spectrum*

Introduction

The mathematical concept of symmetry has multiple practical applications in science and technology. One expression of symmetry is the algebra of the point groups. Molecular physics uses the point group theory for evaluation of some electro-optical parameters. The point group theory is also applied in molecular spectroscopy in order to establish the permitted transitions when the molecule interacts with optical radiations. So, for the molecules belonging to the point groups with small symmetry, the permitted transitions in UV, VIS and IR can be easily established.

The AB_2, C_6H_5-R, or $R-AB_2$ and so far, belong to the low symmetry C_{2v} point group. There are four symmetry operations that transform each from these molecules into itself (Vincent-1977, Landau-1965): reflection in the molecular plane $\sigma_v^{(1)}$, reflection in a plane $\sigma_v^{(2)}$ perpendicular to the molecular plane and rotation with 180^0 around two-fold axis C_2 that is the intersection of the two planes of symmetry, and identity I, operation that does not change anything. These operations do not change the spatial distribution of the nuclei. They must no change the electro-optic parameters of the molecule. It results that the electric dipole moment of the molecules belonging to C_{2v}, must be parallel with the two-fold axis, representing the unchanged direction by all operations of this group of symmetry.

When only the rotation movement is taken into consideration, the molecules ABC_2 and BC_2, are classified depending on the orientation of the molecular electric dipole moment relative to the principal axes of the inertia (Landau - 1965, Herzberg-1945, Eliaşevici-1966).

a). molecules with their two-fold axis parallel to the main axis corresponding to the intermediate value of the inertia moment $(OH_2;SH_2;DH_2)$;

b). molecules with their two-fold axis parallel to the main axis corresponding to the smallest value of the inertia moment ($O-CH_2$-formaldehyde or its derivatives symmetrically substituted).

If the energy levels and their symmetry for the two cases are known, the transitions permitted in the rotational spectrum (in far IR or/and in microwave range) can be easily established. The molecules are considered as asymmetric rigid tops in their electronic ground state (Eliaşevici - 1966).

The case a) of molecules representing rigid tops with their symmetry axis oriented along the axis of the intermediate moment of inertia, such as water, sulphurous hydrogen,...) was studied in (Herzberg - 1945, Dorohoi – 2004).

The molecules OCH_2, OCD_2 or $OCCl_2$ (Eliaşevici -1966, Dorohoi - 2004) have the two-fold axis orientated parallel to the C=O chemical bond and bisecting the angle between the identical chemical bonds. This axis also corresponds to the principal axis of the smallest moment of inertia.

Formaldehyde is a molecule having its two-fold axis along the principal axis of inertia corresponding to the smallest value of the inertia moment. The dipole moment of this molecule is also parallel to the symmetry axis.

The symmetry selection rules for the pure rotations require the same symmetry for the dipole moment variation and the product of the eigenfunctions. It results that the following transitions between the pure rotation levels of formaldehyde are permitted by the symmetry selection rules:

(1). $(+,+)\leftrightarrow(+,-)$ and $(-,-)\leftrightarrow(-,+)$

The dipolar molecules interact with dipolar radiations. So, far IR and microwave absorption induces rotational motions of these molecules. The permitted transitions for the dipolar radiation are given by the selection rule (Herzberg - 1945, Eliaşevici -1966):

(2) $\Delta J = 0, \pm 1$

where J is the quantum number of the kinetic molecular moment, M_p.

$$(3) \qquad M_p^2 = \frac{h^2}{4\pi^2} J(J+1); \quad J = 0, 1, 2, 3, ..$$

The pure rotation energy levels of an asymmetric rigid top can be estimated by using the formula:

$$(4) \qquad E = \frac{1}{2}\left(\frac{M_{pa}^2}{I_a} + \frac{M_{pb}^2}{I_b} + \frac{M_{pc}^2}{I_c} \right)$$

As one can see, rotation energy is an invariant in rapport with the symmetry operations of C_{2v} group.

Usually, one makes the following notations (Eliaşevici -1966, Dorohoi - 2004):

$$(5) \qquad A = \frac{h^2}{8\pi^2 I_a}; \; B = \frac{h^2}{8\pi^2 I_b}; \; C = \frac{h^2}{8\pi^2 I_c}$$

The rotation constants can be expressed in cm^{-1}. In relations (3-5), h is Planck constant, M_{pa}, M_{pb} M_{pc} are the components of the kinetic moment on the main axes oa, ob and oc of inertia. I_a, I_b, I_c signify the main moments of inertia.

Experimentals

Estimation of the main moments of inertia

The estimation of the main moments of inertia for a molecule can be made by using the following relations (Eliaşevici -1966, Dorohoi - 2004):

$$(6) \qquad I_x = \sum_{i=1}^{4} m_i \left(y_i^2 + z_i^2 \right)$$

$$(7) \qquad I_y = \sum_{i=1}^{4} m_i \left(x_i^2 + z_i^2 \right)$$

$$(8) \qquad I_z = \sum_{i=1}^{4} m_i \left(x_i^2 + y_i^2 \right)$$

To easier compare the energy levels of the prolate and oblate tops, the following convention is made: the main axes of the inertia moment are renamed with oa, ob and oc in order of increasing values of the inertia moments. From relation (11) it results that $I_y \geq I_x$ *and* $I_y \geq I_z$. So, the principal axis oc must be taken parallel with oy axis.

The axes oa and ob are taken parallel with ox, respective with oz, if the inequality $I_x \leq I_z$ is satisfied. Contrarily, if $I_x \geq I_z$, the axes oa and ob are taken parallel with oz, respectively with ox.

Energy levels of a molecular asymetric rigid top

In order to estimate the energy for the pure rotation motion of a molecule considered as a rigid asymmetric top, the results of Wang (1929) have been used. The centrifugal distortion of the molecule becomes important for the rapid motions and the supposition about molecular rigidity can not be applied to rotational levels with big J values. Molecules can be considered as rigid tops only for the small values of J. Only rotations corresponding to $J \leq 3$ were taken into consideration in this study.

For the heavy molecules with a great values of I_a, I_b, and I_c (small values of the A, B, C constants), this correction could attend values comparable with the transition wave number. The pure rotation energy levels were computed by using the formula (Dorohoi, 2004):

(9) $$E(J_\tau) = \frac{1}{2}(B+C)J(J+1) + \left[A - \frac{1}{2}(B+C)\right] \cdot W_\tau$$

where W_τ are the solutions of the equations:

(10) J=0: $W_0=0$;

(11) J=1: $W_\tau = 0$ and $W_\tau^2 - 2 \cdot W_\tau + \left(1 - b^2\right) = 0$

(12) J=2: $W_\tau - 1 + 3b = 0$; $W_\tau - 1 - 3b = 0$; $W_\tau - 4 = 0$

$W_\tau^2 - 4 \cdot W_\tau - 12b^2 = 0$

(13) J=3: $W_\tau - 4 = 0$; $W_\tau^2 - 4 \cdot W_\tau - 60b^2 = 0$;

$W_\tau^2 - (10 - 6b) \cdot W_\tau + \left(9 - 54b - 15b^2\right) = 0$

$W_\tau^2 - (10 + 6b) \cdot W_\tau + \left(9 + 54b - 15b^2\right) = 0$

In relations (9)-(13), b signifies:

(14) $$b = \frac{C - B}{2 \cdot \left[A - \frac{1}{2}(B+C)\right]}$$

In order to obtain the energy values for a given J, the (2J+1) equations from (6-11) in unknown term W_τ were solved and the obtained solutions W_τ used in the energy expression (5). The lowest value of W_τ for a given J is noted with W_{-J}, the following lowest, with W_{-J+1}, and so on (Eliaşevici - 1966, Jones -1990).

Computational program

A computational program was made (Dorohoi – 2004). It permits to:

1. estimate the molecular main values of the moments of inertia;
2. estimate the energy of an asymmetric rigid top, having the computed values for the principal moments of inertia;
3. attach the symmetry species for rotations around C_2^a and C_2^c principal axes of moments of inertia;
4. decide what are the permitted transitions in the far IR and microwave spectral ranges, corresponding to a pure rotational motion of the molecule;
5. Attach the statistical weights of rotational levels, permitting the estimation of the intensity of the pure rotational spectral lines.

This program could help spectroscopists to attribute the lines in the pure rotation spectra to a given transition or it can be also used for demonstrative courses, in didactical purposes.

Results and Discussions

Formaldehyde has its two-fold axis (electric dipole moment direction) parallel to the axis of the smallest moment of inertia. Its structural parameters are (Raton-1997): the lengths of the chemical bonds CO=1.23A; CH =1.06A; the angle HCH=123^0; the atomic masses

$$m_O = 26.5586 \cdot 10^{-24}\,g\,, m_C = 20.0979 \cdot 10^{-24}\,g$$

$$m_H = 1.6748 \cdot 10^{-24}\,g\,.$$

Additionally the constant $\frac{h^2}{8h^2}$=27.994 10^{-40} cm^{-1} was considered (Herzberg -1945, Eliaşevici -1966).

The notation and symmetry of the energy levels of formaldehyde are shown in table 1.

Table 1: Dennison's notation and symmetry of the formaldehyde energy levels

J=1	J=2	J=3
1_{-1} (-,+)	2_{-2} (+, +)	3_{-3} (-, +)
1_0 (-,-)	2_{-1} (+, -)	3_{-2} (-, -)
1_1 (+,-)	2_0 (-, -)	3_{-1} (+, -)
	2_1 (-, +)	3_0 (+, +)
	2_2 (+, +)	3_1 (-, +)
		3_2 (-, -)
		3_3 (+, -)

The pure rotation energy levels of formaldehyde were computed (table 2) and their symmetry has been assigned The transitions permitted by relations (1), can be easily established by using symmetry selection rules (Jones, 1990) for the pure rotation spectrum of this molecule, considered as rigid top.

Table 2: Pure rotation energy levels of formaldehyde

J=1	J=2	J=3
2.41	7.23	14.46
10.76	15.43	22.44
10.91	15.88	23.34
	40.93	48.17
	40.94	48.18
		90.29
		90.29

Taking into consideration the symmetry selection rules, expressed by relation (1), the permitted transitions give the wavenumbers of the microwave range which are in a good agreement with the experimental data (Wang-1929, Nielsen - 1931, Randall -1937, Dennison - 1931, Placzek-1933).

Conclusion

The pure rotation spectra of molecules classified to C_{2v} point group of symmetry, having their electric dipolar moment parallel with the axis corresponding to the smallest moment of inertia, can be simulated.

Errors of the results occur in the hypothesis that the molecule is a rigid top, in which the centrifugal distortion is neglected. Experimental evaluation of the magnitude of the term describing centrifugal deformations shall give the possibility to use a correction dependent on the quantum number J and on the structural features of the studied molecule.

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