SYMMETRY PROPERTIES OF THE EFFECTIVE DIPOLE MOMENT OPERATOR AND THE HERMAN-WALLIS FACTOR FOR SYMMETRIC-TOP MOLECULES

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*The symmetry properties of the parameters of the effective dipole moment expressed as a series of vibrational and rotational ladder operators have been investigated for the case of symmetric-top molecules. It is shown that the expression for the Herman-Wallis factor obtained by Watson [J. Mol. Spectrosc. **153**, 211 (1992)] for fundamental bands of symmetric top molecules could be used for overtone, combination, and difference bands in the case of no accidental resonance and if the ℓ-type interaction is negligibly small.*

INTRODUCTION

The expression for the line strengths for both parallel and perpendicular bands in the absence of accidental resonance and if the ℓ-type interaction is negligibly small can be written as

$$W_{\Delta J \Delta K}(J,K) = L_{\Delta J \Delta K}(J,K)\, F_{\Delta J}^{\Delta K}(J,K)\,, \qquad (1)$$

where $L_{\Delta J \Delta K}(J,K)$ is the line strength in the rigid top approximation, the so-called Henl-London factor; whereas $F_{\Delta J}^{\Delta K}(J,K)$ is the correcting Herman-Wallis factor accounting for rovibrational interaction. Watson has shown that the factor written in the form

$$
\begin{aligned}
F_{\Delta J}^{\Delta K}(J,K) = \Big\{ &1 + C^J m_J + C^K m_K + \\
&+ C^{JJ(Q)}\big[\overline{J(J+1)} - m_J^2\big] + C^{JJ(PR)} m_J^2 + \\
&+ C^{KK}\overline{K}^2 + C^{JK} m_J m_K \Big\}^2\,,
\end{aligned}
\qquad (2)
$$

where $\quad m_J = \tfrac{1}{2}\big[J'(J'+1) - J(J+1)\big]\,, \quad \overline{J(J+1)} =$ $= \tfrac{1}{2}\big[J'(J'+1) + J(J+1)\big]\,; \quad m_K = \tfrac{1}{2}[k'^2 - k^2]\,; \quad \overline{K}^2 = \tfrac{1}{2}\big[k'^2 + k^2\big]\,,$ where C^J, C^K, $C^{JJ(Q)}$, $C^{JJ(PR)}$, C^{KK} and C^{JK} are the coefficients dependent on the force field and the dipole moment function, is applicable for linear molecules,[1,2] as well as for fundamental bands of symmetric-top molecules.[3]

The purpose of the present work is to show that the Herman-Wallis factor for overtone, combination, and difference bands of symmetric-top molecules can be written in a similar manner in the case when there is no accidental resonance and the ℓ-type interaction is negligibly small. With this aim in mind, the series of the effective dipole moment operator is written in the most general form in terms of elementary vibrational and rotational ladder operators, and the symmetry properties of the series coefficients are investigated.

EFFECTIVE DIPOLE MOMENT OPERATOR

The line strength corresponding to the transition between the lower n and upper m states is determined as a square matrix element of the dipole moment operator M_Z in the space-fixed coordinate system

$$W_{m \leftarrow n} = 3 \sum_{MM'} \big|< mM' \,|M_Z|\, nM >\big|^2\,. \qquad (3)$$

Here the summation is over the magnetic quantum numbers of the lower M and upper M' rovibrational states, whereas n and m symbolize other quantum numbers. In practice, the method of effective operators[4] is most frequently used for calculation of the matrix elements. In the context of this method, the line strength can be calculated using the following expression:

$$W_{m \leftarrow n} = 3 \sum_{MM'} \Big|< \Psi_{mM'}^{\mathrm{ef}} \,\big|M_Z^{\mathrm{ef}}\big|\, \Psi_{nM}^{\mathrm{ef}} >\Big|^2\,, \qquad (4)$$

where Ψ_{nM}^{ef} are the eigenfunctions of the effective Hamiltonian H^{ef}:

$$H^{\mathrm{ef}} \Psi_{nM}^{\mathrm{ef}} = E_n \Psi_{nM}^{\mathrm{ef}}\,. \qquad (5)$$

The effective Hamiltonian is derived from the rovibrational Hamiltonian H_{VR}, for example, by the method of contact transformations[4,5]:

$$H^{\mathrm{ef}} = \mathrm{e}^{iS_{\mathrm{ct}}}\, H_{VR}\, \mathrm{e}^{-iS_{\mathrm{ct}}}\,, \qquad (6)$$

and, as a consequence, the effective dipole moment

operator can be derived from the molecular dipole moment operator M_Z by the same contact transformations:

$$M_Z^{\text{ef}} = e^{iS_{\text{ct}}} M_Z \, e^{-iS_{\text{ct}}} . \qquad (7)$$

The effective dipole moment operator is the function of vibrational and rotational operators.

Prior to presenting the effective dipole moment operator in the general case, let us choose the molecule-fixed coordinate system and introduce the elementary vibrational and rotational operators. Let us first consider molecules of the C_{NV} ($N \geq 3$) and D_{Nd} ($N \geq 2$) symmetry and then generalize the results to other symmetry groups of the symmetric-top molecules. The above-listed symmetry groups have two generating elements each: rotation C_N^1 by the angle $2\pi/N$ about the N-fold axis (rotation-reflection by the angle π/N about the rotation-reflection $2N$-fold axis) and reflection in the symmetry plane σ_{xz}. Let us choose the molecule-fixed coordinate system in such a way that the z-axis coincides with the principal symmetry axis of the molecule, and the symmetry plane σ_{xz} lies in the coordinate plane xz. Let the bases of the irreducible two-dimensional representations E_q ($q = 1,\dots,[[N/2]]$ for the C_{NV} groups and $q = 1, \dots N-1$ for the D_{Nd} groups) be chosen in such a manner that the matrices corresponding to the generating elements have the form

$$C_N^1 = \begin{pmatrix} \cos\dfrac{2\pi}{N}q & -\sin\dfrac{2\pi}{N}q \\ \sin\dfrac{2\pi}{N}q & \cos\dfrac{2\pi}{N}q \end{pmatrix} \text{ and } \sigma_{xz} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (8)$$

for the C_{NV} symmetry groups, and

$$S_{2N}^1 = \begin{pmatrix} \cos\dfrac{\pi}{N}q & -\sin\dfrac{\pi}{N}q \\ \sin\dfrac{\pi}{N}q & \cos\dfrac{\pi}{N}q \end{pmatrix} \text{ and } \sigma_{xz} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (9)$$

for the D_{Nd} symmetry groups. The normal coordinates $Q_{t_q a}$ and $Q_{t_q b}$ of the degenerate vibration t_q of the E_q symmetry are oriented along the x and y axes, respectively. Note that both the C_{3V} and D_{2d} symmetry groups have one two-dimensional representation $E \equiv E_1$. The above-used designation $[[N/2]]$ is for the integer part of $N/2$.

The ladder vibrational operators $^{t_q}A_\tau^\pm$ for the degenerate vibration t_q of the E_q symmetry are defined by the expressions:

$$^{t_q}A_\pm^+ = a_{t_q a}^+ \pm i a_{t_q b}^+ , \qquad (10)$$

$$^{t_q}A_\pm^- = a_{t_q a} \pm i a_{t_q b} , \qquad (11)$$

where $a_{t_q \alpha}^+$ and $a_{t_q \alpha}$ ($\alpha = a, b$) are the operators of creation and annihilation of vibrational quanta with a frequency ω_{t_q}. With the appropriate phase choice of the wave functions (see Ref. 6) an action of the ladder operators on the wave functions of the two-dimensional harmonic oscillator is described by the following relations:

$$A_\pm^+ | V \ell > = \mp\sqrt{V \pm \ell + 2} \, | V + 1 \, \ell \pm 1 > , \qquad (12)$$

$$A_\pm^- | V \ell > = \pm\sqrt{V \mp \ell} \, | V - 1 \, \ell \pm 1 > . \qquad (13)$$

The subscript t_q is omitted here for the sake of simplicity.

The ladder operators of the angular momentum components are introduced as

$$J_\pm = J_x \mp i J_y . \qquad (14)$$

With the Shortli-Condon phase choice, action of these ladder operators on the eigenfunctions $| JK >$ of the rigid symmetric top is defined as follows:

$$J_\pm | JK > = \sqrt{(J \mp K)(J \pm K + 1)} \, | JK \pm 1 > ; \qquad (15)$$

$$J_z | JK > = K \, | JK > . \qquad (16)$$

Let us turn to the ladder operators

$$\begin{aligned} \lambda_+ &= \lambda_Z^x - i \, \lambda_Z^y , \\ \lambda_- &= \lambda_Z^x + i \, \lambda_Z^y , \\ \lambda_0 &= \lambda_Z^z \end{aligned} \qquad (17)$$

of the direction cosines λ_z^α connecting the molecule-fixed coordinate system with the space-fixed one. Note that the matrix elements of the direction cosines λ_+, λ_-, and λ_0 in the basis of eigenfunctions of the rigid symmetric top are nonzero only for $\Delta K = 1, -1$, and 0, respectively.

In the case of symmetric-top molecules, using the above-introduced elementary vibrational and rotational operators, the effective dipole moment operator in the explicitly Hermitian form and in the most general case can be presented as

$$M_Z^{\text{ef}} = \sum_{\substack{\text{over} \\ \text{all indices}}} \left\{ M_\tau^{\dots\{mnk\ell\}_{t_q}\dots\{de\}_s\dots \, gfh} \times \right.$$

$$\times \prod_{t_q} (^{t_q}A_+^+)^m (^{t_q}A_-^+)^n (^{t_q}A_-^-)^k (^{t_q}A_+^-)^\ell \times$$

$$\times \prod_{s} (a_s^+)^d (a_s)^e \ \Phi_\tau^{gfh} + \big(M_\tau^{\cdots \{mnk\ell\}_{t_q} \cdots \{de\}_s \cdots gfh} \big)^* \times$$

$$\times \prod_{t_q} (^{t_q}A_+^+)^k (^{t_q}A_-^+)^\ell (^{t_q}A_-^-)^m (^{t_q}A_+^-)^n \times$$

$$\times \prod_{s} (a_s^+)^e (a_s)^d (\Phi_\tau^{gfh})^+ \Big\}, \tag{18}$$

where $\tau = 1, -1, 0$;

$$\Phi_1^{gfh} = J^{2g} \ [\lambda_+, \ J_+^f (2J_z + f)^h]_+ \ ;$$

$$\Phi_{-1}^{gfh} = J^{2g} \ [\lambda_+, \ (2J_z + f)^h J_-^f]_+ \quad (f > 0) \ ;$$

$$\Phi_0^{gfh} = J^{2g} \ [\lambda_0, \ J_+^f (2J_z + f)^h]_+ \ . \tag{19}$$

The subscripts t_q and s are used in Eq. (18) for numbering the degenerate and non-degenerate vibrations, respectively. The signs $(\ldots)^*$ and $(\ldots)^+$ are used for complex and Hermitian conjugation.

SYMMETRY PROPERTIES OF THE PARAMETERS

The dipole moment operator and, consequently, the effective dipole moment operator are the real ones. Hence, the effective dipole moment operator must be invariant with respect to time reversal operation, which consists of sign alteration of time and the complex conjugation of its coefficients. This requirement imposes the condition upon the parameters of the effective dipole moment

$$\big(M_\tau^{\cdots \{mnk\ell\}_{t_q} \cdots \{de\}_s \cdots gfh} \big)^* =$$

$$= (-1)^{f+h} \big(M_\tau^{\cdots \{\ell knm\}_{t_q} \cdots \{ed\}_s \cdots gfh} \big)^*, \tag{20}$$

which can be derived with the use of the transformation properties of the elementary vibrational and rotational operators presented in the Table I.

TABLE I. Transformation properties of the elementary operators.

Operator	Hermitian conjugation	Time reversal	C_N^1 rotation	S_{2N}^1 mirror rotation	Reflection in the σ_{xz} plane
$^{t_q}A_\tau^\pm$	$^{t_q}A_{-\tau}^\mp$	$^{t_q}A_{-\tau}^\pm$	$e^{-\frac{2\pi i}{N}q\tau t_q} A_\tau^\pm$	$e^{-\frac{\pi i}{N}q\tau t_q} A_\tau^\pm$	$^{t_q}A_{-\tau}^\pm$
$a_{A_1}^\pm$	$a_{A_1}^\mp$	$a_{A_1}^\pm$	$a_{A_1}^\pm$	$a_{A_1}^\pm$	$a_{A_1}^\pm$
$a_{A_2}^\pm$	$a_{A_2}^\mp$	$a_{A_2}^\pm$	$a_{A_2}^\pm$	$a_{A_2}^\pm$	$-a_{A_2}^\pm$
$a_{B_1}^\pm$	$a_{B_1}^\mp$	$a_{B_1}^\pm$	$-a_{B_1}^\pm$	$-a_{B_1}^\pm$	$a_{B_1}^\pm$
$a_{B_2}^\pm$	$a_{B_2}^\mp$	$a_{B_2}^\pm$	$-a_{B_2}^\pm$	$-a_{B_2}^\pm$	$-a_{B_2}^\pm$
J_τ	$J_{-\tau}$	$-J_{-\tau}$	$e^{+\frac{2\pi i}{N}\tau} J_\tau$	$-e^{+\frac{\pi i}{N}\tau} J_\tau$	$-J_{-\tau}$
J_z	J_z	$-J_z$	J_z	J_z	$-J_z$
λ_τ	$\lambda_{-\tau}$	$\lambda_{-\tau}$	$e^{+\frac{2\pi i}{N}\tau} \lambda_\tau$	$-e^{+\frac{\pi i}{N}\tau} \lambda_\tau$	$-\lambda_{-\tau}$
λ_z	λ_z	λ_z	λ_z	λ_z	$-\lambda_z$

If the molecular symmetry group has the generating element σ_{xz}, then this results in the additional condition on the effective dipole moment parameters. According to the Hougen (Ref. 7) and Longuet-Higgins (Ref. 8) scheme, reflection in the σ_{xz} plane is equivalent a certain permutation of the identical nuclei followed by the space inversion at the origin of the coordinates (P^*). Hence it follows that the effective dipole moment operator must change the sign under the action of this operation:

$$\sigma_{xz} M_Z^{\text{ef}} = -M_Z^{\text{ef}} \ . \tag{21}$$

Let us first assume that all one-dimensional normal vibrations in a molecule are fully symmetric with respect to the reflection in a plane. Then, taking into account the transformation properties of the elementary vibrational and rotational operators presented in the Table I, the requirement (21) leads to the following condition for the parameters of the effective dipole moment operator:

$$(M_\tau^{\ldots\{mnk\ell\}_{t_q}\ldots\{de\}_s\ldots gfh})^* =$$

$$= (-1)^{f+h}(M_\tau^{\ldots\{\ell knm\}_{t_q}\ldots\{ed\}_s\ldots gfh}) . \qquad (22)$$

Comparing the expressions (20) and (22), we can find

$$M_\tau^{\ldots\{\ell knm\}_{t_q}\ldots\{ed\}_s\ldots gfh} = (M_\tau^{\ldots\{\ell knm\}_{t_q}\ldots\{ed\}_s\ldots gfh})^* , \qquad (23)$$

that means that the parameters are real. It can be shown that if a molecule has the one-dimensional normal vibrations antisymmetric with respect to σ_{xz}, then the parameters of the effective dipole moment operator are real for the terms with the even total power of the elementary vibrational operators antisymmetric with respect to σ_{xz} and these parameters are imaginary otherwise.

Let us investigate the behavior of the effective dipole moment operator with respect to the C_N^1 rotation. In the Hougen[7] and Longuet–Higgins[8] scheme, this transformation is equivalent to the pure permutation of the identical nuclei (P). The effective dipole moment operator must be invariant with respect to the permutation of the identical nuclei, hence

$$C_N^1 M_Z^{\mathrm{ef}} = M_Z^{\mathrm{ef}} . \qquad (24)$$

Let consider an arbitrary term in Eq. (18) and suppose for simplicity that the subscript s is only for vibrations, which are antisymmetric with respect to the C_N^1 operation, i.e. for the B-type vibrations. Then, according to the transformation properties of the elementary vibrational and rotational operators (see the Table), under the action of the C_N^1 rotation, this term is multiplied by the factor

$$\exp\left(-\frac{2\pi i}{N}\left\{\sum_{t_q} q[(m+\ell)_{t_q} - (n+k)_{t_q}] -\right.\right.$$

$$\left.\left. - r + \frac{N}{2}\sum_s (d-e)_s \right\}\right), \qquad (25)$$

where

$$r = 1 + f \text{ at } \tau = 1 ,$$
$$r = 1 - f \text{ at } \tau = -1 , \qquad (26)$$
$$r = f \text{ at } \tau = 0 .$$

In order to fulfil the relation (24), the expression in parenthesis in Eq. (25) must be a multiple of $2\pi i$. This requirement leads to the condition

$$\sum_{t_q} q[(m+\ell)_{t_q} - (n+k)_{t_q}] - r = N(p - \tfrac{1}{2}\sum_s (d-e)_s) ,$$

$$p = 0, \pm 1, \pm 2,\ldots \qquad (27)$$

whence, with regard for Eqs. (12), (13), (15), and (16) and the comments following Eq. (17), we obtain the selection rules for the matrix elements of the effective dipole moment operator

$$\sum_{t_q} q\,\Delta\ell_{t_q} - \Delta K = N\left(p - \frac{1}{2}\sum_s \Delta V_s\right) ,$$

$$p = 0, \pm 1, \pm 2,\ldots , \qquad (28)$$

where V_s are the quantum numbers of the nondegenerate B-type vibrations.

If a symmetry group has the S_{2N}^1 rotation-reflection as the generating element instead of the C_N^1 rotation, then Eqs. (27) and (28) are somewhat modified. Indeed, in the Hougen[7] and Longuet–Higgins[8] scheme, the rotation-reflection S_{2N}^1 corresponds to some permutation with inversion P^*. Hence, the effective dipole moment operator must be antisymmetric with respect to the rotation-reflection

$$S_{2N}^1 M_Z^{\mathrm{ef}} = -M_Z^{\mathrm{ef}} . \qquad (29)$$

Performing the considerations analogous to the previous ones, i.e. accounting for Eq. (29) and the transformation properties of the elementary vibrational and rotational operators with respect to the S_{2N}^1 operation (see the Table), we obtain the following condition on the powers of the operators belonging to an arbitrary term in Eq. (18):

$$\sum_{t_q} q\left[(m+\ell)_{t_q} - (n+k)_{t_q}\right] - r = 2N\left(p - \frac{1}{2}\left[r + \sum_s (d-e)_s\right]\right) , \qquad (30)$$

where $p = 0, \pm 1, \pm 2, \ldots$ is an arbitrary integer number; r is given by Eq. (26); and the subscript s is used only for vibrations antisymmetric with respect to S_{2N}^1, i.e. for the B-type vibrations. The following selection rules for the matrix elements of the effective dipole moment operator result from Eq. (30) for the symmetry groups having the rotation-reflection operation S_{2N}^1 as the generating element:

$$\sum_{t_q} q\,\Delta\ell_{t_q} - \Delta K = 2N\left\{p - \frac{1}{2}\left(\Delta K + \sum_s \Delta V_s\right)\right\} , \qquad (31)$$

where $p = 0, \pm 1, \pm 2, \ldots , V_s$ are the quantum numbers

of nondegenerate B-type vibrations. Note that the selection rules (28) and (31) were discussed in Ref. 9 by Papoušek, however, our expression (31) differs from the analogous one presented in Ref. 9. The selection rules analogous to those presented by Eqs. (28) and (31), but for the matrix elements of the effective Hamiltonian, are derived in Ref. 10.

The results presented in this Section for the symmetry groups C_{NV} and D_{Nd} can be easily generalized to the C_N and S_{2N} symmetry groups, respectively. Since the latter ones have only one generating element C_N^1 (or S_{2N}^1), the parameters of the effective dipole moment given by Eq. (18), are complex values, and Eqs. (27) and (28) (or Eqs. (30) and (31) for the S_{2N} group) remain valid.

All the results obtained for the C_{NV} and C_N symmetry groups automatically could be applied to the D_{Nh} and C_{Nh} symmetry groups, respectively. For the latter ones it is necessary only to take into account the additional selection rules connected with the additional generating element σ_h (reflection in the plane perpendicular to the principal axis) or I (inversion). Let assume that the symmetry group under consideration has an inversion. Then, taking into account the fact that the effective dipole moment operator changes the sign under the action of this operation, whereas all rotational operators are invariant with respect to it, we arrive to the condition: the total power of the vibrational operators of the «u» symmetry in Eq. (18) must be odd. Since the effective dipole moment operator likewise changes the sign under the action of the σ_h operation, and the rotational operators transform as

$$\sigma_h J_z = J_z, \ \sigma_h J_\tau = -J_\tau, \ (\tau = +, \ -),$$

$$\sigma_h \lambda_z = \lambda_z, \ \sigma_h \lambda_\tau = -\lambda_\tau, \ (\tau = +, \ -), \tag{32}$$

we obtain the following condition for the D_{Nh} and C_{Nh} symmetry groups having no inversion: the total even power of the ladder operators J_τ and λ_τ in Eq. (18) must correspond to the total odd power of the vibrational operators of the «″» symmetry, and, quite the reverse, the total odd power of the ladder operators must correspond to the total even power of the vibrational operators of the «″» symmetry.

Due to isomorphism of the C_{NV} and D_N groups, all the results obtained for the C_{NV} group automatically could be applied to the D_N group provided that the molecule-fixed coordinate systems are chosen properly. The full correspondence is achieved by orientation of the y-axis of the molecule-fixed coordinate system along the two-fold U axis of the D_N group provided that in the case of the C_{NV} group the symmetry plane lies in the coordinate plane xz.

HERMAN-WALLIS FACTOR

As noted above, the Herman–Wallis factor is introduced to account for rovibrational interactions in the intensities calculations of the "allowed" transitions in the rigid top approximation. In this approximation, the rotational part of the M_Z^{ef} operator consists of the direction cosines only, that results in the selection rules $\Delta K = 0, \pm 1$. Therefore, the terms in Eq. (18) contributing into intensities of the above-mentioned transitions must satisfy the following condition:

$$r = 0, \ \pm 1,$$

where r is introduced by Eq. (26). Owing to Eq. (27) (or Eq. (30) for the molecules of the S_{2N} and D_{Nd} symmetry), these terms for a certain ΔK (in other words, for a certain r) and a certain band have the same vibrational operator, which is independent of the τ subscript of the rotational operators M_τ^{gfh}. This allows us to introduce the Herman–Wallis factor independent of vibrational quantum numbers for any "allowed" band. Another consequence of the relationship (27) (or Eq. (30)) is that a set of rotational operators (19) forming the Herman–Wallis factor for an "allowed" parallel ($\Delta K = 0$) or perpendicular ($\Delta K = \pm 1$) band does not depend on whether this band is fundamental, overtone, or difference. Therefore, the expression for the Herman–Wallis factor obtained in Ref. 3 for fundamental bands automatically could be applied to other bands of the above-listed types. Certainly, each band has its own values of the parameters of the Herman-Wallis factor.

CONCLUSION

In the present paper, the effective dipole moment operator for the symmetric-top molecules derived within the framework of the conventional formulation of the method of contact transformations is written in the general case in terms of the rising and lowering ladder vibrational and rotational operators. The symmetry properties of its parameters are established. The selection rules for the matrix elements of this operator in the basis of the eigenfunctions of harmonic oscillators and the rigid symmetric top rotor are presented. These results are sufficient to allow the conclusion that the Herman-Wallis factor in the form obtained by Watson in Ref. 3 for the fundamental bands of molecules under consideration is applicable for overtone, combination, and difference bands in the case when there are no accidental resonances and the ℓ-type interactions are negligibly small.

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