Improved model of the effective dipole moments and absolute ro-vibrational line strengths of the XY$_2$ asymmetric top molecules in the X^2B_1 doublet electronic states

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A new effective dipole moment model for the (XY$_2$ symmetry) molecule in a doublet electronic state is derived that includes (as special cases) all currently known models of effective dipole moment for such type molecules, and allows, at the same time, to take into account an influence of spin-rotation interactions on the effective dipole moment operator which were not taken into account in the preceding studies.

Keywords: asymmetric top molecules in non-singlet electronic states, spin-rotation interactions, absolute line strengths, effective dipole moment operator.

1. Introduction

The problem of correct characterization of absolute strengths of ro-vibrational lines in polyatomic molecules has historically remained one of the most important ones in high-resolution molecular spectroscopy. It has been discussed countless times in spectroscopic literature on different types of polyatomic molecules [1–5]. The ones presenting the greatest challenge in this context are asymmetric top molecules [6–8]. As an illustration of this, we cite just one of the seminal works of Flaud and Camy-Peyret [1] who obtained the effective dipole moment in the general form for two types of bands of an XY$_2$ molecule (with symmetry C_{2v}) and its matrix elements on eigen functions of the corresponding effective operators. The results of this study are being used widely to this day by different research groups in the examination of absolute strengths of various XY$_2$ molecules and (improved results of [1]) more complex asymmetric top molecules. Being unable to recapitulate properly a wealth of research in this field, we cite here only several studies [9–13] that have been published in recent years by the authors of the present report.

Speaking of the „landmark" work [1] and other similarly themed studies cited above, one should note that all of them were focused on asymmetric top molecules in so-called singlet electronic states. At the same time, even the simplest asymmetric top molecules (XY$_2$ with symmetry C_{2v}) may exist in nature not only in singlet, but also in multiplet electronic states (an example is provided by free radicals NO$_2$ and ClO$_2$, which have doublet state X^2B_1 as their ground electronic state). Both the effective dipole moment theory and calculations of absolute strengths of

lines for such molecules are significantly more complex and differ from the models and calculations for „traditional" molecules. The development of the corresponding theory for molecules in doublet electronic states has been progressing since the 1980s [14–17]. However, it still cannot be said that all the needed effects (including those of the same order of magnitude as the ones present in models) have been taken into account. Specifically, it is evident that a correct model of the effective dipole moment operator should include not only purely rotational centrifugal effects, which are the manifestations of ro-vibrational interactions in molecules, but also spin-rotation corrections, which, in turn, are the manifestations of spin-ro-vibrational effects. This is understood easily if one remembers that the influence of spin-ro-vibrational interactions (see [18–34] and recent studies [35–37]) on the effective Hamiltonian (and, consequently, ro-vibrational energies) is of the same order of magnitude as the influence of common ro-vibrational interactions. It is to be expected that this trend should also persist in the effective dipole moment operator. However, the influence of spin-rotation interactions on absolute line strengths in all studies published to date has been tracked only via the influence on spin-rotation functions, which are the eigen functions of the corresponding effective operators. The direct effect of spin-ro-vibrational interactions on the effective dipole moment operator has not been examined yet in literature. In the present study, this effect is taken into consideration, a more correct (compared to the one that is still being used in literature) effective dipole moment operator is obtained, and band ν_3 of a ClO$_2$ molecule is used as an example to demonstrate that spin-rotation interactions taken into account directly in the effective dipole moment

operator may exert a significantly more profound influence on absolute strengths than spin-rotation interactions factored in via wave functions.

2. Effective dipole moment models and absolute transition strengths in XY$_2$ molecules with symmetry C_{2v}

It is common knowledge that the absolute strength of a ro-vibrational line of a molecule (in the present case, an XY$_2$ molecule with symmetry C_{2v}) is given by

$$S_{v_0}^N = \frac{8\pi^3 v_0}{4\pi\epsilon_0 3hc} \left[1 - \exp\left(-\frac{hcv_0}{k_B T} \right) \right]$$

$$\times \frac{g_i}{Z(T)} \exp\left(-\frac{E_i}{k_B T} \right) \mathscr{R}_i^f . \quad (1)$$

Since the quantities used in expression (1) were discussed in detail, e.g., in [1], these explanations are omitted here. We focus on $\mathscr{R}_i^f$, which is the squared matrix element of the so-called effective dipole moment operator of a molecule on ro-vibrational wave functions of states of the examined transition and presents the greatest difficulty in calculations of absolute strengths. Thorough clarifying descriptions of the already available models of the effective dipole moment and the approaches to calculation of its matrix elements are omitted here for brevity. Let us just outline three major approaches to the issue of determination of the effective dipole moment operator for an XY$_2$ molecule (with symmetry C_{2v}) and then characterize the fourth one, which is the method developed in the present study, in more detail in the next section. The simplest model (I) of the effective dipole moment operator postulates that both ro-vibrational and spin-rotation interactions are lacking in a molecule. „Effective" dipole moment operator P_Z is then reduced to simple form $P_Z = k_{Z\alpha}$, $\alpha = x, y, z$; $k_{Z\alpha}$ are elements of the direction cosine matrix (matrix of transition from a spatially fixed reference frame to a molecule-fixed one) for a rigid asymmetric top [8]. It is well known that the $k_{Z\alpha}$ operator matrix elements take the form

$$< Jk \mid k_{Zz} \mid Jk > = k \left\{ \frac{(2J+1)}{J(J+1)} \right\}^{1/2} , \quad (2)$$

$$< Jk \mid k_{Zx} \mid Jk \pm 1 > = \pm < Jk \mid ik_{Zy} \mid Jk \pm 1 >$$

$$= \frac{1}{2} \left\{ \frac{(2J+1)(J \mp k)(J \pm k + 1)}{J(J+1)} \right\}^{1/2} , \quad (3)$$

$$< Jk \mid k_{Zz} \mid J+1k > = \left\{ \frac{(J+k+1)(J-k+1)}{(J+1)} \right\}^{1/2} , \quad (4)$$

$$< Jk \mid k_{Zx} \mid J+1k \pm 1 > = \pm < Jk \mid ik_{Zy} \mid J+1k \pm 1 >$$

$$= \mp \frac{1}{2} \left\{ \frac{(J \pm k + 1)(J \pm k + 2)}{(J+1)} \right\}^{1/2} , \quad (5)$$

$$< Jk \mid k_{Zz} \mid J-1k > = \left\{ \frac{(J+k)(J-k)}{J} \right\}^{1/2} , \quad (6)$$

$$< Jk \mid k_{Zx} \mid J-1k \pm 1 > = \pm < Jk \mid ik_{Zy} \mid J-1k \pm 1 >$$

$$= \pm \frac{1}{2} \left\{ \frac{(J \mp k)(J \mp k - 1)}{J} \right\}^{1/2} . \quad (7)$$

A more rigorous model (II), which was considered in [{]1 and is applicable to molecules in a singlet electronic state, includes ro-vibrational interactions in a molecule (i.e., takes into account centrifugal contributions to the effective dipole moment operator). The length of this report being limited, we do not present the results obtained with model (II); the reader may find them in Table II in [1]. The third „iteration" of the effective dipole moment operator model was formulated for a molecule in a doublet electronic state. That said, the model developed in [14–17] has been used up until now to characterize the absolute strengths of spin-ro-vibrational transitions in molecules of this kind. Spin-rotation interactions are taken into account in this model only in terms of their influence on spin-ro-vibrational wave functions that are the solution of a Schrödinger equation with effective Hamiltonians of vibrational states the transitions between which are considered. At the same time, only purely rotational „centrifugal effects," which are the manifestations of ro-vibrational interactions in molecules, are taken into account in the effective dipole moment operator itself. Spin-rotation centrifugal corrections, which may emerge due to the presence of spin-ro-vibrational interactions, are ignored. It was demonstrated in [38] that each ro-vibrational molecular line is split within this model into several components with their absolute strengths given by

$$\mathscr{R}_{(NJk)}^{(\widetilde{N}\,\widetilde{J}\,\widetilde{k})} = g(NJ, \widetilde{N}\widetilde{J}) \mathscr{R}_{(Jk)}^{(\widetilde{J}\,\widetilde{k})}, \quad (8)$$

where (in the notation adopted in [14–17]) quantum number N corresponds to the sum of rotational and spin angular momenta; $\mathscr{R}_{(Jk)}^{(\widetilde{J}\,\widetilde{k})}$ and $\mathscr{R}_{(NJk)}^{(\widetilde{N}\,\widetilde{J}\,\widetilde{k})}$ are the matrix elements of the effective dipole moment operator in models II and III (on ro-vibrational and spin-ro-vibrational functions, respectively); and $g(NJ, \widetilde{N}\widetilde{J})$ are the coefficients specifying the relative strength of components into which each ro-vibrational transition is split due to spin-rotation interactions. Performing transformations similar to those discussed in the next section of the present study, one finds that coefficients $g(NJ, \widetilde{N}\widetilde{J})$ have the form presented in Table 1. The values of coefficients $g(NJ, \widetilde{N}\widetilde{J})$ from [38] differ from the doubled values of coefficients from Table 1 by fractions of a percent, providing almost completely matching relative strengths of splitting components for all ro-vibrational transitions. At the same time, it may be noted that the sums of values in the last column of Table 1 for each of the three types of ro-vibrational transitions are very close to unity (in [38], they are close to 2). Thus, the coefficients in Table 1 may be

regarded as coefficients of distribution of absolute strengths of ro-vibrational transitions over their spin-rotation components.

3. Improved model (IV) of the effective dipole moment of a molecule with the dependence on spin-ro-vibrational interactions factored in

With no possibility to provide a detailed account of the derivations here, we note only that the Schrödinger equation for the effective Hamiltonian assumes the following form if spin-ro-vibrational interactions in a molecule are characterized correctly:

$$\widetilde{H} \mid v', R_i(Nk, SJ)\rangle = \delta_{vv'} E^{(v)}_{v, R_i(Nk,SJ)} \mid v, R_i(Nk, SJ)\rangle$$

$$= \delta_{vv'} E^{(v)}_{v, R_i(Nk, SJ)} \mid v\rangle \mid R_i(Nk, SJ)\rangle, \quad (9)$$

and the squared matrix element of the effective dipole moment operator in formula (1) may be written as

$$\mathscr{R}^{(\widetilde{v},\ \widetilde{R}_j(\widetilde{N}\ \widetilde{k},\ S\ \widetilde{J}))}_{(v, R_i(Nk, SJ))} =$$

$$= \left| (\langle J| \otimes \langle S|)^N_k \| \langle v \mid \left(G^+ P^{(1)} G \right)^1 \mid \widetilde{v}\rangle \| \left(|\widetilde{J}\rangle \otimes |S\rangle \right)^{\widetilde{N}}_{\widetilde{k}} \right|^2 =$$

$$= \left| (\langle J| \otimes \langle S|)^N_k \sum_{\alpha} \left\{ \frac{1}{2} k^{\Gamma}_{Z\alpha}\ {}^{(\alpha)}\mu^{\widetilde{\Gamma}}_{\text{rot}} + {}^{(\alpha)}\mu^{\widetilde{\Gamma}}_{\text{sp-rot}} \right\}^{\gamma}_{+} (|\widetilde{J}\rangle \otimes |S\rangle)^{\widetilde{N}}_{\widetilde{k}} \right|^2, \quad (10)$$

where $\gamma = (\Gamma \times \widetilde{\Gamma})$. The right-hand side of expression (10) features two terms. The first one corresponds to the approximation of model III. The second term was neglected in previous studies, although it may be demonstrated (see also Section 6 of the present study) that its contributions to the end result are comparable in magnitude to the contributions of the first term. As above, we skip intermediate calculations and proceed directly to the analysis of the influence of this second term on two major types of absorption bands in molecules with axial symmetry C_{3v}.

4. Parallel ro-vibrational bands

It may be demonstrated that index γ in expression (10) is equal to A_2 in this case and (with an accuracy up to the contributions that are small relative to expressions (2)–(7)) the following five operators should be taken into account in the second term of effective dipole moment operator (10):

$$\left\{ \sum_{\alpha} k^{\Gamma}_{Z\alpha},\ \mu^{\widetilde{\Gamma}}_{\text{sp-rot}} \right\}^{A_2}_{+} = \left\{ k_{Zx},\ \widetilde{\mu}^{(v-\widetilde{v})}_1 (R \cdot S) + \widetilde{\mu}^{(v-\widetilde{v})}_2 (R_z S_z) \right.$$

$$\left. + \widetilde{\mu}^{(v-\widetilde{v})}_3 (R_x S_x - R_y S_y) \right\}_{+} + \left\{ k_{Zy},\ \widetilde{\mu}^{(v-\widetilde{v})}_4 (R_x S_y + R_y S_x) \right\}_{+}$$

$$+ \left\{ k_{Zz},\ \widetilde{\mu}^{(v\widetilde{v})}_5 (R_x S_z + R_z S_x) \right\}_{+}. \quad (11)$$

The matrix elements of five operators from formula (11) on ro-vibrational functions $(|J\rangle \otimes |S\rangle)^N_k$ take the form

$$(\langle J| \otimes \langle S|)^N_k \left\{ k_{Zx},\ \widetilde{\mu}^{(v-\widetilde{v})}_1 (R \cdot S) \right\}_{+} \left(|\widetilde{J}\rangle \otimes |S\rangle \right)^{\widetilde{N}}_{\widetilde{k}}$$

$$= \mu^{(v-\widetilde{v})}_1 \sqrt{\widetilde{g}(NJ, \widetilde{N}\widetilde{J})}\ \langle Jk|k_{Zx}|\widetilde{J}\ \widetilde{k}\rangle \Big[\widetilde{J}(\widetilde{J} + 1)$$

$$- \widetilde{N}(\widetilde{N} + 1) + J(J + 1) - N(N + 1) - 2S(S + 1) \Big], \quad (12)$$

where $\widetilde{k} = k \pm 1$ and $\mu^{(v-\widetilde{v})}_1$ is a rewritten (multiplied by an insignificant constant) $\widetilde{\mu}^{(v-\widetilde{v})}_1$ parameter. The matrix elements of the next two operators are

$$(\langle J| \otimes \langle S|)^N_k \left\{ k_{Zx},\ \widetilde{\mu}^{(v-\widetilde{v})}_2 (R_z S_z) \right\}_{+} \left(|\widetilde{J}\rangle \otimes |S\rangle \right)^{\widetilde{N}}_{\widetilde{k}}$$

$$= \mu^{(v-\widetilde{v})}_2 \sqrt{\widetilde{g}(NJ, \widetilde{N}\widetilde{J})}\ \langle Jk|k_{Zx}|\widetilde{J}\ \widetilde{k}\rangle$$

$$\times \left\{ \frac{k^2}{N(N + 1)} \Big[J(J + 1) - N(N + 1) - S(S + 1) \Big] \right.$$

$$\left. + \frac{\widetilde{k}^2}{\widetilde{N}(\widetilde{N} + 1)} \Big[\widetilde{J}(\widetilde{J} + 1) - \widetilde{N}(\widetilde{N} + 1) - S(S + 1) \Big] \right\}, \quad (13)$$

where $\widetilde{k} = k \pm 1$,

$$(\langle J| \otimes \langle S|)^N_k \left\{ k_{Zx},\ \widetilde{\mu}^{(v-\widetilde{v})}_3 (R_x S_x - R_y S_y) \right\}_{+} \left(|\widetilde{J}\rangle \otimes |S\rangle \right)^{\widetilde{N}}_{\widetilde{k}}$$

$$= \mu^{(v-\widetilde{v})}_3 \sqrt{\widetilde{g}(NJ, L\widetilde{J})}\ \langle Jk|k_{Zx}|\widetilde{J}\ l\rangle \Bigg\{ \left(\langle \widetilde{J}| \otimes \langle S| \right)^L_l$$

$$\times \left[\left(R^{(1)} \otimes S^{(1)} \right)^2_2 + \left(R^{(1)} \otimes S^{(1)} \right)^2_{-2} \right] \left(|\widetilde{J}\rangle \otimes |S\rangle \right)^{\widetilde{N}}_{\widetilde{k}} \Bigg\}$$

$$+ \mu^{(v-\widetilde{v})}_3 \Bigg\{ (\langle J| \otimes \langle S|)^N_k \left[\left(R^{(1)} \otimes S^{(1)} \right)^2_2 + \left(R^{(1)} \otimes S^{(1)} \right)^2_{-2} \right]$$

$$\times (|J\rangle \otimes |S\rangle)^M_m \Bigg\} \sqrt{\widetilde{g}(MJ, \widetilde{N}\widetilde{J})}\ \langle Jm|k_{Zx}|\widetilde{J}\ \widetilde{k}\rangle, \quad (14)$$

the last expression holds true both at $(\widetilde{k} = k \pm 1)$ and at $\widetilde{k} = k \pm 3$, and nonzero matrix elements of the operators found in (14) take the form

$$(\langle J| \otimes \langle S|)^N_k \left(R^{(1)} \otimes S^{(1)} \right)^2_{\pm 2} (|J\rangle \otimes |S\rangle)^N_{k = k \mp 2}$$

$$= (-1)^{2(N-J)} \frac{(2N + 1)}{4J(2J + 1)}$$

$$\times \{ (N \pm k - 1)(N \pm k)(N \mp k + 1)(N \mp k + 2) \}^{1/2}, \quad (15)$$

Table 1. Nonzero values of coefficients $\widetilde{g}(NJ, \widetilde{N}\widetilde{J})$ („relative strengths") of spin-rotation components of rotational transitions

$\widetilde{N}$	$\widetilde{J}$	J	$\Delta J = \widetilde{J} - J$	Value
$\widetilde{N} = N - 1$	$\widetilde{J} = \widetilde{N} + 1/2 = N - 1/2$	$J = N + 1/2$	$\Delta J = \Delta N$	$\frac{2N-1}{4N}$
	$\widetilde{J} = \widetilde{N} - 1/2 = N - 3/2$	$J = N - 1/2$	$\Delta J = \Delta N$	$\frac{2N+1}{4N}$
	$\widetilde{J} = \widetilde{N} + 1/2 = N - 1/2$	$J = N - 1/2$	$\Delta J \neq \Delta N$	$\frac{1}{4N^2}$
	$\widetilde{J} = \widetilde{N} - 1/2 = N - 3/2$	$J = N + 1/2$	$\Delta J \neq \Delta N$	0
$\widetilde{N} = N$	$\widetilde{J} = N + 1/2$	$J = N + 1/2$	$\Delta J = \Delta N$	$\frac{N(2N+3)}{4(N+1)^2}$
	$\widetilde{J} = N - 1/2$	$J = N - 1/2$	$\Delta J = \Delta N$	$\frac{(N+1)(2N-1)}{4N^2}$
	$\widetilde{J} = N - 1/2$	$J = N + 1/2$	$\Delta J \neq \Delta N$	$\frac{1}{4N(N+1)}$
	$\widetilde{J} = N + 1/2$	$J = N - 1/2$	$\Delta J \neq \Delta N$	$\frac{1}{4N(N+1)}$
$\widetilde{N} = N + 1$	$\widetilde{J} = \widetilde{N} + 1/2 = N + 3/2$	$J = N + 1/2$	$\Delta J = \Delta N$	$\frac{2N+1}{4(N+1)}$
	$\widetilde{J} = \widetilde{N} - 1/2 = N + 1/2$	$J = N - 1/2$	$\Delta J = \Delta N$	$\frac{2N+3}{4(N+1)}$
	$\widetilde{J} = \widetilde{N} - 1/2 = N + 1/2$	$J = N + 1/2$	$\Delta J \neq \Delta N$	$\frac{1}{4(N+1)^2}$
	$\widetilde{J} = \widetilde{N} + 1/2 = N + 3/2$	$J = N - 1/2$	$\Delta J \neq \Delta N$	0

and

$$
(\langle J| \otimes \langle S|)_k^N \left(R^{(1)} \otimes S^{(1)} \right)_{\pm 2}^2 (|J\rangle \otimes |S\rangle)_{\widetilde{k}=k\mp 2}^{(N+\Delta N)} = \frac{\Delta N(k-\widetilde{k})}{4}
$$
$$
\times \left\{ \frac{(N\pm k)(N\mp k+1)[(N+1)+\Delta N(2\mp k)][N+\Delta N(2\mp k)]}{(2J+1)(2J+2+\Delta N)} \right\}^{1/2}. \tag{16}
$$

Having analyzed expressions (14)–(16), one may draw an important inference that, in addition to possible quantum number variations $\widetilde{k} = k \pm 1$ and $\widetilde{N} = N \pm 1$, these expressions allow $\widetilde{k} = k \pm 3$ and $\widetilde{N} = N, N\pm$). The following is obtained for the last two operators in expression (11) for the effective dipole moment:

$$
(\langle J| \otimes \langle S|)_k^N \left\{ k_{Zy}, \ \widetilde{\mu}_4^{(v-\widetilde{v})}(R_x S_y + R_y S_x) \right\}_+ \left(|\widetilde{J}\rangle \otimes |S\rangle \right)_{\widetilde{k}}^{\widetilde{N}}
$$
$$
= \mu_4^{(v-\widetilde{v})} \sqrt{\widetilde{g}(NJ, M\widetilde{J})} \ \langle Jk|k_{Zx}|\widetilde{J}\,l\rangle (l-k) \left\{ \left(\langle \widetilde{J}| \otimes \langle S| \right)_l^M \right.
$$
$$
\times \left. \left[\left(R^{(1)} \otimes S^{(1)} \right)_2^2 - \left(R^{(1)} \otimes S^{(1)} \right)_{-2}^2 \right] \left(|\widetilde{J}\rangle \otimes |S\rangle \right)_{\widetilde{k}}^{\widetilde{N}} \right\}
$$
$$
+ \mu_4^{(v-\widetilde{v})} \sqrt{\widetilde{g}(NJ, M\widetilde{J})} \ \langle Jk|k_{Zx}|\widetilde{J}\,l\rangle (l-k) \left\{ \left(\langle \widetilde{J}| \otimes \langle S| \right)_l^M \right.
$$
$$
\times \left. \left[\left(R^{(1)} \otimes S^{(1)} \right)_2^2 - \left(R^{(1)} \otimes S^{(1)} \right)_{-2}^2 \right] \left(|\widetilde{J}\rangle \otimes |S\rangle \right)_{\widetilde{k}}^{\widetilde{N}} \right\}, \tag{17}
$$

$$
(\langle J| \otimes \langle S|)_k^N \left\{ k_{Zx}, \ \widetilde{\mu}_5^{(v-\widetilde{v})}(R_x S_z + R_z S_x) \right\}_+ \left(|\widetilde{J}\rangle \otimes |S\rangle \right)_{\widetilde{k}}^{\widetilde{N}}
$$
$$
= \mu_5^{(v-\widetilde{v})} \sqrt{\widetilde{g}(NJ, L\widetilde{J})} \ \langle Jk|k_{Zx}|\widetilde{J}\,l\rangle \left\{ \left(\langle \widetilde{J}| \otimes \langle S| \right)_l^L \right.
$$
$$
\times \left. \left[\left(R^{(1)} \otimes S^{(1)} \right)_{-1}^2 - \left(R^{(1)} \otimes S^{(1)} \right)_1^2 \right] \left(|\widetilde{J}\rangle \otimes |S\rangle \right)_{\widetilde{k}}^{\widetilde{N}} \right\}
$$
$$
+ \mu_5^{(v-\widetilde{v})} \left\{ (\langle J| \otimes \langle S|)_k^N \left[\left(R^{(1)} \otimes S^1 \right)_{-1}^2 - \left(R^{(1)} \otimes S^{(1)} \right)_1^2 \right] \right.
$$
$$
\times (|J\rangle \otimes |S\rangle)_m^M \left. \right\} \sqrt{\widetilde{g}(MJ, \widetilde{N}\widetilde{J})} \ \langle Jm|k_{Zx}|\widetilde{J}\,\widetilde{k}\rangle, \tag{18}
$$

where

$$
(\langle J| \otimes \langle S|)_k^N \left(R^{(1)} \otimes S^{(1)} \right)_{\pm 1}^2 (|J\rangle \otimes |S\rangle)_{\widetilde{k}=k\mp 1}^N
$$
$$
= (-1)^{2(N-J)} \frac{(2N+1)(1\mp 2k)}{4J(2J+1)} \left\{ (N\pm k)(N\mp k+1) \right\}^{1/2}, \tag{19}
$$

$$
(\langle J| \otimes \langle S|)_k^N \left(R^{(1)} \otimes S^{(1)} \right)_{\pm 1}^2 (|J\rangle \otimes |S\rangle)_{\widetilde{k}=k\mp 1}^{(N+\Delta N)}
$$
$$
= \frac{\Delta N(k-\widetilde{k})(N\mp 2k+1)}{4} \left\{ \frac{(N\mp k+1)[N+\Delta N(2\mp k)]}{(2J+1)(2J+2+\Delta N)} \right\}^{1/2}. \tag{20}
$$

5. Perpendicular ro-vibrational bands

Index γ in formula (10) is equal to E in this case, and it can be seen that five operators again need to be taken into account in the second term of effective dipole moment operator (10), although these five differ from the ones for parallel bands:

$$
\begin{aligned}
\left\{\sum_\alpha k_{Z\alpha}^{\Gamma}, \mu_{\text{sp-rot}}^{\widetilde{\Gamma}}\right\}_+^{B_2} &= \left\{k_{Zz},\ \widetilde{\mu}_1^{(v-\widetilde{v})}(R\cdot S) + \widetilde{\mu}_2^{(v-\widetilde{v})}(R_z S_z)\right. \\
&\left. + \widetilde{\mu}_3^{(v-\widetilde{v})}(R_x S_x - R_y S_y)\right\}_+ \\
&+ \left\{k_{Zy},\ \widetilde{\mu}_4^{(v-\widetilde{v})}[(R_y S_z + R_z S_y)]\right\}_+ \\
&+ \frac{1}{2}\left\{k_{Zx},\ \widetilde{\mu}_5^{(v-\widetilde{v})}[(R_x S_z + R_z S_x)]\right\}_+ .
\end{aligned}
\tag{21}
$$

Proceeding in the same way as in the previous section, one finds

$$
\begin{aligned}
&\left(\langle J|\otimes\langle S|\right)_k^N \left\{k_{Zz},\ \widetilde{\mu}_1^{(v-\widetilde{v})}(R\cdot S)\right\}_+ \left(|\widetilde{J}\rangle\otimes|S\rangle\right)_{\widetilde{k}}^{\widetilde{N}} \\
&= \mu_1^{(v-\widetilde{v})}\sqrt{\widetilde{g}(NJ,\widetilde{N}\widetilde{J})}\ \langle Jk|k_{Zz}|\widetilde{J}\,\widetilde{k}\rangle\Big[\widetilde{J}(\widetilde{J}+1) - \widetilde{N}(\widetilde{N}+1) \\
&\quad + J(J+1) - N(N+1) - 2S(S+1)\Big],
\end{aligned}
\tag{22}
$$

$$
\begin{aligned}
&\left(\langle J|\otimes\langle S|\right)_k^N \left\{k_{Zz},\ \widetilde{\mu}_2^{(v-\widetilde{v})}(R_z S_z)\right\}_+ \left(|\widetilde{J}\rangle\otimes|S\rangle\right)_{\widetilde{k}}^{\widetilde{N}} \\
&= \mu_2^{(v-\widetilde{v})}\sqrt{\widetilde{g}(NJ,\widetilde{N}\widetilde{J})}\ \langle Jk|k_{Zz}|\widetilde{J}\,\widetilde{k}\rangle \\
&\quad \times\left\{\frac{k^2}{N(N+1)}[J(J+1) - N(N+1) - S(S+1)]\right. \\
&\quad \left. + \frac{\widetilde{k}^2}{\widetilde{N}(\widetilde{N}+1)}\left[\widetilde{J}(\widetilde{J}+1) - \widetilde{N}(\widetilde{N}+1) - S(S+1)\right]\right\},
\end{aligned}
\tag{23}
$$

where $\widetilde{k} = k$;

$$
\begin{aligned}
&\left(\langle J|\otimes\langle S|\right)_k^N \left\{k_{Zz},\ \widetilde{\mu}_3^{(v-\widetilde{v})}(R_x S_x - R_y S_y)\right\}_+ \left(|\widetilde{J}\rangle\otimes|S\rangle\right)_{\widetilde{k}}^{\widetilde{N}} \\
&= \mu_3^{(v-\widetilde{v})}\sqrt{\widetilde{g}(NJ,L\widetilde{J})}\ \langle Jk|k_{Zz}|\widetilde{J}\,k\rangle\Big\{\left(\langle\widetilde{J}|\otimes\langle S|\right)_{l=k}^L \\
&\quad \times\left[\left(R^{(1)}\otimes S^{(1)}\right)_2^2 + \left(R^{(1)}\otimes S^{(1)}\right)_{-2}^2\right]\left(|\widetilde{J}\rangle\otimes|S\rangle\right)_{\widetilde{k}}^{\widetilde{N}}\Big\} \\
&\quad + \mu_3^{(v-\widetilde{v})}\Big\{\left(\langle J|\otimes\langle S|\right)_k^N\left[\left(R^{(1)}\otimes S^{(1)}\right)_2^2 + \left(R^{(1)}\otimes S^{(1)}\right)_{-2}^2\right] \\
&\quad \times \left(|J\rangle\otimes|S\rangle\right)_{m=\widetilde{k}}^M\Big\}\sqrt{\widetilde{g}(MJ,\widetilde{N}\widetilde{J})}\times \langle J\widetilde{k}|k_{Zz}|\widetilde{J}\,\widetilde{k}\rangle,
\end{aligned}
\tag{24}
$$

$$
\begin{aligned}
&\left(\langle J|\otimes\langle S|\right)_k^N \left\{k_{Zy},\ \widetilde{\mu}_4^{(v-\widetilde{v})}(R_y S_z + R_z S_y)\right\}_+ \left(|\widetilde{J}\rangle\otimes|S\rangle\right)_{\widetilde{k}}^{\widetilde{N}} \\
&= \mu_4^{(v-\widetilde{v})}(l-k)\sqrt{\widetilde{g}(NJ,L\widetilde{J})}\ \langle Jk|k_{Zx}|\widetilde{J}\,l\rangle\Big\{\left(\langle\widetilde{J}|\otimes\langle S|\right)_l^L \\
&\quad \times\left[\left(R^{(1)}\otimes S^{(1)}\right)_{-1}^2 + \left(R^{(1)}\otimes S^{(1)}\right)_1^2\right]\left(|\widetilde{J}\rangle\otimes|S\rangle\right)_{\widetilde{k}}^{\widetilde{N}}\Big\} \\
&\quad + \mu_4^{(v-\widetilde{v})}(\widetilde{k}-m)\Big\{\left(\langle J|\otimes\langle S|\right)_k^N\left[\left(R^{(1)}\otimes S^{(1)}\right)_{-1}^2\right. \\
&\quad \left. + \left(R^{(1)}\otimes S^{(1)}\right)_1^2\right]\left(|J\rangle\otimes|S\rangle\right)_m^M\Big\}\sqrt{\widetilde{g}(MJ,\widetilde{N}\widetilde{J})}\langle Jm|k_{Zx}|\widetilde{J}\,\widetilde{k}\rangle,
\end{aligned}
\tag{25}
$$

$$
\begin{aligned}
&\left(\langle J|\otimes\langle S|\right)_k^N \left\{k_{Zy},\ \widetilde{\mu}_5^{(v-\widetilde{v})}(R_x S_z + R_z S_x)\right\}_+ \left(|\widetilde{J}\rangle\otimes|S\rangle\right)_{\widetilde{k}}^{\widetilde{N}} \\
&= \mu_5^{(v-\widetilde{v})}\sqrt{\widetilde{g}(NJ,L\widetilde{J})}\ \langle Jk|k_{Zy}|\widetilde{J}\,l\rangle\Big\{\left(\langle\widetilde{J}|\otimes\langle S|\right)_l^L \\
&\quad \times\left[\left(R^{(1)}\otimes S^{(1)}\right)_{-1}^2 - \left(R^{(1)}\otimes S^{(1)}\right)_1^2\right]\left(|\widetilde{J}\rangle\otimes|S\rangle\right)_{\widetilde{k}}^{\widetilde{N}}\Big\} \\
&\quad + \mu_5^{(v-\widetilde{v})}\Big\{\left(\langle J|\otimes\langle S|\right)_k^N\left[\left(R^{(1)}\otimes S^{(1)}\right)_{-1}^2 - \left(R^{(1)}\otimes S^{(1)}\right)_1^2\right] \\
&\quad \times \left(|J\rangle\otimes|S\rangle\right)_m^M\Big\}\sqrt{\widetilde{g}(MJ,\widetilde{N}\widetilde{J})}\ \langle Jm|k_{Zy}|\widetilde{J}\,\widetilde{k}\rangle.
\end{aligned}
\tag{26}
$$

Quantum numbers $\widetilde{N}$ and $\widetilde{k}$ in the last three expressions may assume the values of $\Delta N = \widetilde{N} - N = 0, \pm1, \pm2$ and $\Delta k = \widetilde{k} - k = 0, \pm2$.

6. Illustration: a fragment of the ν_3 band of a $^{35}\text{ClO}_2$ molecule

To illustrate the validity and importance of the obtained results, we present here a small fragment of the spectrum (a series of „forbidden" transitions with $\Delta k = -2$) of the ν_3 band of a $^{35}\text{ClO}_2$ free radical for the lowest values of quantum number k (see the figure). The lowest k values were chosen for the fact that the corresponding transitions provide the most vivid demonstration of the necessity of application of improved (compared to model III) model IV in order to perform a correct analysis of experimental data. Analyzing the results presented in Section 5, one sees readily that the values of matrix elements corresponding to Q transitions decrease as $\frac{k}{\sqrt{N}}$ with increasing quantum number N, while the values of matrix elements corresponding to P and R transitions increase as $\left(\frac{N^2-k^2}{\sqrt{N}}\right)$. This is the reason why we present a short series of „forbidden" R transitions as an illustration in Table 2 and the figure; signs „+" and „–" in the first column of Table 2 correspond to two different components of spin-rotation doublets, the experimental line positions and transmittance in columns 3 and 4 were taken from [37],

Table 2. Illustration of the „forbidden" $\Delta k = -2$ transitions in band ν_3 of a $^{35}ClO_2$ molecule

Transition			$\nu_{calc},$ cm^{-1}	$\nu_{meas},$ cm^{-1}	Transmittance, %
$[N\prime = N+1\ K_a' = 0\ K_c'\ (\sigma')]$	$-$	$[N\ K_a = 2\ K_c\ (\sigma)]$			
1			2	3	4
$[4\ 0\ 4\ (-)]$	$-$	$[3\ 2\ 1\ (-)]$	1106.7267	1106.7262	92
$[4\ 0\ 4\ (+)]$	$-$	$[3\ 2\ 1\ (+)]$	1106.7824	1106.7828	92
$[6\ 0\ 6\ (-)]$	$-$	$[5\ 2\ 3\ (-)]$	1107.7978	1107.7976	95
$[6\ 0\ 6\ (+)]$	$-$	$[5\ 2\ 3\ (+)]$	1107.8319	1107.8315	89
$[8\ 0\ 8\ (-)]$	$-$	$[7\ 2\ 5\ (-)]$	1108.6547	1108.6546	86
$[8\ 0\ 8\ (+)]$	$-$	$[7\ 2\ 5\ (+)]$	1108.6882	covered	62
$[10\ 0\ 10\ (-)]$	$-$	$[9\ 2\ 7\ (-)]$	1109.1992	1109.2000	80
$[10\ 0\ 10\ (+)]$	$-$	$[9\ 2\ 7\ (+)]$	1109.2575	covered	61
$[12\ 0\ 12\ (-)]$	$-$	$[11\ 2\ 9\ (-)]$	1109.3568	1109.3563	85
$[12\ 0\ 12\ (+)]$	$-$	$[11\ 2\ 9\ (+)]$	1109.4050	1109.4050	80
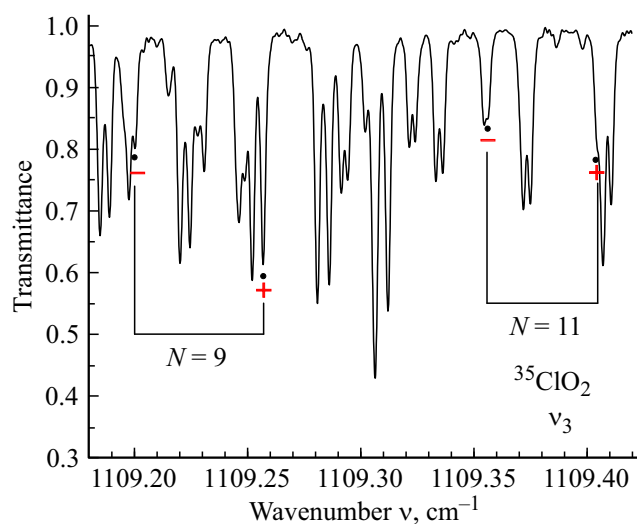
Small fragment of the experimental spectrum of a ClO_2 molecule from [37]. „Forbidden" $\Delta k = -2$ transitions are denoted by dark circles. The experimental conditions are as follows: spectral resolution — 0.0015 cm^{-1}; number of scans — 400; radiation source — Globar; detector — MCT313; KBr beam splitter; optical path length — 0.23 m; aperture — 1.15 mm; temperature — 22.0±0.3°C; pressure — 100 Pa; CO_2 and H_2O lines were used for calibration.

and the predicted positions of „forbidden" transitions were calculated with parameters also taken from [37]. It can be seen that the indicated transitions are fairly strong and are even on par in terms of strength with „allowed" transitions (not shown in the figure). The reader might argue that these transitions may be produced in the spectrum by a superposition of basis wave functions within the well-known model III; however, actual calculations demonstrate that the potential contributions of such superpositions to absolute strengths of the examined lines are incomparably smaller than the contributions of the discussed effects in model IV.

7. Conclusions

A new model of the effective dipole moment of an asymmetric top molecule in a doublet electronic state was developed. The general form of matrix elements of the obtained effective dipole moment operators, which are needed to characterize correctly the absolute strengths of spin-ro-vibrational transitions in molecules of this kind, for both parallel and perpendicular bands was determined. The derived expressions allow one both to include higher-order corrections for „allowed" transitions and to characterize weak „forbidden" transitions.

Conflict of interest

The authors declare that they have no conflict of interest.

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