Collisional "Selection Rules" for Asymmetric Top Molecules

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(Z. Naturforsch. **32 a**, 614–619 [1977]; received March 19, 1977)

Selection rules for collision-induced rotational transitions of asymmetric top molecules are derived by first order perturbation treatment. The theoretical results are in agreement with the results from four-level double resonance experiments in the microwave range.

Introduction

Four-level microwave double resonance experiments provide information about selection rules and rates for collision-induced transitions between rotational levels of molecules in gas phase, a topic which has been reviewed by Oka[1]. So far, only a few experiments on rotationally inelastic collisions of asymmetric top molecules have been performed in the microwave range[2–6]. The results suggest a preference of dipolar collisional "selection rules" in many cases. In this paper we will give some theoretical arguments to support this experimental evidence.

Theory

The subsequent theoretical treatment of molecular rotationally inelastic collisions is based upon several assumptions. At first, only bimolecular collisions are considered. Collisions which involve more than two molecules are more than six orders of magnitude less probable at the usual experimental pressure (<100 mT) and temperature conditions ($-70\,^\circ$C to $+20\,^\circ$C).

For the classification of intermolecular events the concept of strong and weak collisions has proved to be useful. We restrict ourselves to the limiting case of weak collisions which implies small intermolecular interaction energies of long range. Weak collisions may be characterized in terms of molecular dimensions by assuming that the collisional impact parameter is large with respect to the sum of the van der Waals radii of the colliding molecules, i. e. no essential overlapping of the charge distribution of the molecules occurs. When treating the translational motion of the molecules classically which is generally believed to be feasible[7a], the classical path is usually approximated to be linear in the weak collision limit[7b]. This is due to the fact that the translational motion is not appreciably affected in its energy by the smaller changes in rotational energies.

We consider only rotationally inelastic collisions and may treat for weak collisions the intermolecular potential as a small perturbation to the unperturbed effective rotational Hamiltonian of the two colliding molecules. We limit our discussion to a first order time dependent perturbation treatment i. e. to collisions where the time integral over the intermolecular potential is small as compared to $\hbar$. For many molecules this approach should lead to reasonable results for impact parameters in the range from typically 30 to 100 Å.

With the above assumptions we get in first order approximation for the probability that the colliding molecules undergo a transition from initial state $E^{\mathrm{i}}_{R_1} + E^{\mathrm{i}}_{R_2}$ to final state $E^{\mathrm{f}}_{R_1} + E^{\mathrm{f}}_{R_2}$ (see Ref. [1, 7a]):

$$P_{R_1{}^{\mathrm{i}} R_2{}^{\mathrm{i}} \to R_1{}^{\mathrm{f}} R_2{}^{\mathrm{f}}} = \left| \frac{1}{\hbar} \int\limits_{-\infty}^{+\infty} \langle R_1{}^{\mathrm{i}} R_2{}^{\mathrm{i}} | V(t) | R_1{}^{\mathrm{f}} R_2{}^{\mathrm{f}} \rangle \, e^{i \Delta E_{\mathrm{R}} t/\hbar} \, \mathrm{d}t \right|^2 \qquad (1)$$

where R designates rotational states of the colliding molecules (1 and 2), ΔE_R is the change of the total rotational energy due to the collision ($\Delta E_R = E^{\mathrm{f}}_{R_1} + E^{\mathrm{f}}_{R_2} - E^{\mathrm{i}}_{R_1} - E^{\mathrm{i}}_{R_2}$, $\ll kT$ in the weak collision limit), and $V(t)$ is the time-dependent intermolecular potential. The binary collision model used to derive (1) implies that the average collision time is short with respect to the average time between collisions (impact approximation)[8]. The time dependence enters via the center of mass motion of the colliding molecules which is treated classically so that time enters parametrically into the Hamiltonian. In order to obtain collisional "selection rules" in first order approximation it is sufficient to consider only the matrix element

$$V_{\mathrm{if}}(t) = \langle R_1{}^{\mathrm{i}} R_2{}^{\mathrm{i}} | V(t) | R_1{}^{\mathrm{f}} R_2{}^{\mathrm{f}} \rangle \qquad (2)$$

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in Equation (1). The initial and final state wave functions $|R_1{}^{\mathrm{i}} R_2{}^{\mathrm{i}}\rangle$, $|R_1{}^{\mathrm{f}} R_2{}^{\mathrm{f}}\rangle$ are products of the eigenfunctions of the unperturbed rotational Hamiltonian of the colliding molecules. Depending on the type of collision partner they involve eigenfunctions of linear, symmetric or asymmetric top molecules. Rotational eigenfunctions of linear molecules can be treated as a special case of symmetric rotor eigenfunctions ($K=0$). Introductory to the derivation of selection rules for collision-induced transfer of rotational energy of asymmetric rotors we will summarize the results presented by Oka[1] for symmetric top molecules. When considering only Coulomb interaction of the two colliding molecules we have:

$$V(t)=\sum_{i,k} q_i\, q_k / r_{ik}(t)\,. \qquad (3)$$

The distance of electron or nucleus i with charge q_i of molecule 1 to electron or nucleus k with charge q_k of molecule 2 is denoted by $r_{ik}(t)$.

The intermolecular potential (3) can be rewritten for non-overlapping charge distributions in terms of spherical harmonics Y_{lm}[9]:

$$\begin{aligned} V(t) &= 4\pi \sum_{l_1 l_2} \sum_{m_1 m_2} C_{l_1 l_2}\, C(l_1\, l_2\, l, m_1\, m_2\, \overline{m}) \\ &\times \frac{Y^{*}_{l\overline{m}}[\Theta(t), \Phi(t)]}{R(t)^{l+1}} \sum_{i,k} q_i\, q_k\, r_i{}^{l_1}\, r_k{}^{l_2}\, Y_{l_1 m_1}(\Theta_i, \Phi_i) \\ &\times Y_{l_2 m_2}(\Theta_k, \Phi_k) \end{aligned} \qquad (4)$$

with $l=l_1+l_2$.

$\mathbf{R}=(R, \Theta, \Phi)$ vector of magnitude R connecting the center of mass of molecule 1 (CM_1) to center of mass of molecule 2 (CM_2);

$\boldsymbol{r}_j=(r_j, \Theta_j, \Phi_j)$ position vector of magnitude r_j of charge q_j ($j=i, k$) relative to CM_1 and CM_2 respectively;

(Θ, Φ) and (Θ_j, Φ_j) ($j=i, k$) give the angular orientations of $\mathbf{R}$, $\boldsymbol{r}_i$ and $\boldsymbol{r}_k$ with respect to the space-fixed axis system X, Y, Z.

$C(l_1\, l_2\, l, m_1\, m_2\, \overline{m})$ Clebsch-Gordon coefficients[10] with $\overline{m}=m_1+m_2$,

$$C_{l_1 l_2}=\frac{(-1)^{l_2}}{2\,l+1}\left\{\frac{4\pi\,(2\,l+1)\,!}{(2\,l_1+1)\,!\;(2\,l_2+1)\,!}\right\}^{1/2}.$$

We may now transform the spherical harmonics $Y_{l_1 m_1}(\Theta_i, \Phi_i)$ and $Y_{l_2 m_2}(\Theta_k, \Phi_k)$ in (4) from the space-fixed axis system X, Y, Z: (F) to a molecule-fixed axis system x, y, z: (g), for example given by the molecular principal axes a, b, c. If $(\Theta_{j_0}, \Phi_{j_0})$ [$j=i$ or k respectively] denotes the angular orientation of $\boldsymbol{r}$ [$\boldsymbol{r}_i$ or $\boldsymbol{r}_k$] with respect to the molecule-orientated axis system, then

$$Y_{lm}(\Theta_j, \Phi_j)=\sum_{m'=-l}^{l} D^{l}_{m' m}(\alpha\, \beta\, \gamma)\, Y_{lm'}(\Theta_{j_0}, \Phi_{j_0}) \qquad (5)$$

where $D^{l}_{m' m}(\alpha\, \beta\, \gamma)$ is a matrix element of the rotation operator with Eulerian angles α, β and γ that relates the orientation of the molecule-fixed axes to that of the space-fixed axes *. Defining the molecular multipole moments $M_{lm'}$

$$M_{lm'}=\sum_{j} q_j\, r_j{}^{l}\, Y_{lm'}(\Theta_{j_0}, \Phi_{j_0})\,, \quad j=i, k \qquad (6)$$

which are molecular quantities, and substituting (5) and (6) in (4) we have:

$$\begin{aligned} V(t) &= 4\pi \sum_{l_1 l_2} \sum_{m_1 m_2} C_{l_1 l_2}\, C(l_1\, l_2\, l, m_1\, m_2\, \overline{m}) \\ &\times \frac{Y^{*}_{l\overline{m}}[\Theta(t), \Phi(t)]}{R(t)^{l+1}} \sum_{m_1' m_2'} D^{l_1}_{m_1' m_1}(\alpha_1\, \beta_1\, \gamma_1) \\ &\times D^{l_2}_{m_2' m_2}(\alpha_2\, \beta_2\, \gamma_2)\, M_{l_1 m_1'}\, M_{l_2 m_2'} \end{aligned} \qquad (7)$$

with $l=l_1+l_2$.

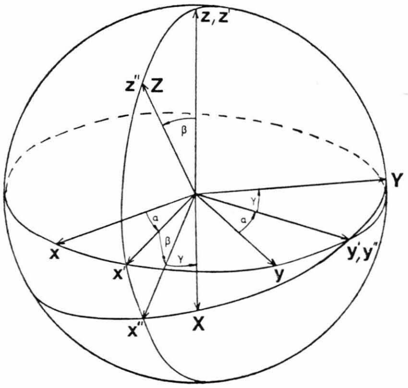

Fig. 1. Definition of the Eulerian angles α, β, γ.

The multipole moments – so far treated classically – have to be replaced in accordance with the use of an effective rotational Hamiltonian by the averages over the respective ground vibronic states, in the following written as $\hat{M}_{lm'}$. The interaction potential as given in (7) contains only contributions from permanent multipole. Second order potential interaction terms such as induction and dispersion interaction are not considered here.

Substituting (7) in (2) with symmetric rotor functions $|JKM\rangle$ for the two colliding molecules the

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* With the definition of the rotation matrix and the Eulerian angles according to Rose[11], the molecule-fixed axis system is transformed into the space-fixed axis system by successive application of α, β and γ (see Figure 1).

important part for the derivation of collisional selection rules is given by

$$\hat{M}_{l_1 m_1'} \langle J_1{}^{\mathrm{i}} K_1{}^{\mathrm{i}} M_1{}^{\mathrm{i}} \,|\, D^{l_1}_{m_1' m_1}(\alpha_1 \beta_1 \gamma_1) \,|\, J_1{}^{\mathrm{f}} K_1{}^{\mathrm{f}} M_1{}^{\mathrm{f}} \rangle \quad (8)$$
$$\times \hat{M}_{l_2 m_2'} \langle J_2{}^{\mathrm{i}} K_2{}^{\mathrm{i}} M_2{}^{\mathrm{i}} \,|\, D^{l_2}_{m_2' m_2}(\alpha_2 \beta_2 \gamma_2) \,|\, J_2{}^{\mathrm{f}} K_2{}^{\mathrm{f}} M_2{}^{\mathrm{f}} \rangle \,.$$

We may now investigate only one of the two factors in (8) (assuming the other to be nonzero) and omit for simplicity the index (1 or 2) labelling the collisional partners. The discussion of the second factor would follow the same lines of thought. As the rotation matrix elements are eigenfunctions of the symmetric rotor[12]

$$|J K M\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} D^{J}_{KM}(\alpha \beta \gamma)$$
$$= \left(\frac{2J+1}{8\pi^2}\right)^{1/2} e^{-iK\alpha}\, \mathrm{d}^{J}_{KM}(\beta)\, e^{-iM\gamma} \quad (9)$$

we can conclude by examining their products in (8) that the transition $J^{\mathrm{i}} K^{\mathrm{i}} M^{\mathrm{i}} \rightarrow J^{\mathrm{f}} K^{\mathrm{f}} M^{\mathrm{f}}$ may occur if[1]:

$$\begin{aligned} \Delta M &= M^{\mathrm{f}} - M^{\mathrm{i}} = m\,, && |m| \leqq l \\ \Delta K &= K^{\mathrm{f}} - K^{\mathrm{i}} = m'\,, && |m'| \leqq l \\ \Delta J &= |J^{\mathrm{f}} - J^{\mathrm{i}}| \leqq l\,, && \text{and } J^{\mathrm{i}} + J^{\mathrm{f}} \geqq l\,. \end{aligned} \quad (10)$$

The collisional selection rules (10) hold for nonvanishing multipole moments $\hat{M}_{lm'}$.

Whether the $\hat{M}_{lm'} = \langle 0 | M_{lm'} | 0 \rangle$ are zero is known from symmetry considerations. $|0\rangle$ denotes the totally symmetric ground vibronic state. Only those moments $M_{lm'}$ have to be considered which belong to the totally symmetric species of the point group of the molecules[13]. The influence of the configuration symmetry is explicitly shown below when deriving collisional selection rules for asymmetric top molecules.

For asymmetric rotors, the selection rules (10) hold for the rotational quantum numbers J and M. This follows immediately from the fact that the asymmetric rotor functions are linear combinations of symmetric rotor functions with the same J and M:

$$|J K_- K_+ M\rangle = \sum_K a^{K_- K_+}_{JKM} |J K M\rangle\,. \quad (11)$$

K_- and K_+ are pseudo quantum numbers corresponding to the quantum numbers of the limiting prolate and oblate symmetric top[14]. In order to obtain collisional selection rules for $K_- K_+$ we have to consider the matrix element

$$\langle J^{\mathrm{i}} K_-{}^{\mathrm{i}} K_+{}^{\mathrm{i}} M^{\mathrm{i}} \,|\, D^{l}_{m'm}(\alpha \beta \gamma) \,|\, J^{\mathrm{f}} K_-{}^{\mathrm{f}} K_+{}^{\mathrm{f}} M^{\mathrm{f}} \rangle \quad (12)$$

which will be discussed using symmetry arguments. The asymmetric rotor functions may be classified by the parity of K_- and K_+ according to the irreducible representation of the Four-group[15], see Table 1.

Table 1. Character Table of the Four-group V (a, b, c) (e = even, o = odd); a, b, and c denote the molecular principal inertia axes with a the axis of least and c the axis of greatest moment of inertia.

Symmetry species	Operations E	$C_2{}^a$	$C_2{}^b$	$C_2{}^c$	Parity of $K_- K_+$
A	1	1	1	1	ee
B_a	1	1	−1	−1	eo
B_b	1	−1	1	−1	oo
B_c	1	−1	−1	1	oe

To classify the matrix element (12) with respect to the Four-group species we have to symmetrize the rotation matrix elements $D^{l}_{m'm}(\alpha \beta \gamma)$. Remembering the fact that $D^{l}_{m'm}(\alpha \beta \gamma)$ is related to the symmetric rotor functions according to (9) this symmetrization may be performed by introducing Wang-type functions[16], a procedure which is common in the asymmetric rotor problem.

Let

$$S^{l}_{m'm\varrho}(\alpha \beta \gamma)$$
$$= \frac{1}{\sqrt{2}} [D^{l}_{m'm}(\alpha \beta \gamma) + (-1)^{\varrho} D^{l}_{-m'm}(\alpha \beta \gamma)] \quad \text{for } m' > 0 \quad (13\,\mathrm{a})$$

with

$$\varrho = 0, 1$$

and

$$S^{l}_{0m}(\alpha \beta \gamma) = D^{l}_{0m}(\alpha \beta \gamma) \quad \text{for } m' = 0\,. \quad (13\,\mathrm{b})$$

Then, referred to a molecule-fixed x, y, z system * with quantization axis z, the symmetrized functions $S^{l}_{m'm\varrho}(\alpha \beta \gamma)$ transform like:

$$\begin{aligned} \mathrm{E}&: S^{l}_{m'm\varrho} \rightarrow S^{l}_{m'm\varrho}\,, \\ \mathrm{C}_2{}^x&: S^{l}_{m'm\varrho} \rightarrow (-1)^{l+m'+\varrho} S^{l}_{m'm\varrho}\,, \\ \mathrm{C}_2{}^y&: S^{l}_{m'm\varrho} \rightarrow (-1)^{l+\varrho} S^{l}_{m'm\varrho}\,, \\ \mathrm{C}_2{}^z&: S^{l}_{m'm\varrho} \rightarrow (-1)^{m'} S^{l}_{m'm\varrho}\,. \end{aligned} \quad (14)$$

To derive (14) the transformation properties of $d^{l}_{m'm}(\beta)$ according to Edmonds[17] have been used.

The relationship to the species of the Four-group $V(x, y, z)$ is given by the even or odd character of $l + \varrho$ and m', see Table 2. The symmetry classification with respect to $V(a, b, c)$ depends on the cor-

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* We choose here the general x, y, z-system because the choice of the correlation between the x, y, z- and a, b, c axes may simplify the symmetry considerations (see the example given later).

relation of x, y, z with a, b, c. The rotation matrix elements $D^l_{m'm}(\alpha\beta\gamma)$ in (12) may be written, using (13 a)

$$D^l_{m'm}(\alpha\beta\gamma) = \frac{1}{\sqrt{2}}\,[S^l_{m'm1}(\alpha\beta\gamma) + S^l_{m'm0}(\alpha\beta\gamma)] \quad \text{for } m' \neq 0. \tag{15}$$

With (13 b) and (15) the $D^l_{m'm}(\alpha\beta\gamma)$ are expressed by the symmetrized functions $S^l_{m'm\varrho}(\alpha\beta\gamma)$. They are the basis functions of reducible representations of $V(x, y, z)$ which contain, according to Table 2 the following irreducible representations:

$$\begin{array}{ll} A + B_z & \text{for } m' \neq 0, \text{ even} \\ B_y + B_x & \text{for } m' \neq 0, \text{ odd} \end{array} \tag{16 a}$$

irrespective of the parity of l, and

$$\begin{array}{ll} A & \text{for } m' = 0, l \text{ even}, \\ B_z & \text{for } m' = 0, l \text{ odd}. \end{array} \tag{16 b}$$

If the matrix element (12) is not to vanish its product species * must contain after reduction the totally symmetric species A of V. This gives with (16) for nonzero $M_{lm'}$ the selection rules

$$\begin{array}{l} A \leftrightarrow A,\ B_x \leftrightarrow B_x,\ B_y \leftrightarrow B_y,\ B_z \leftrightarrow B_z, \\ B_z \leftrightarrow A,\ B_x \leftrightarrow B_y \\ \text{for } m' \neq 0, \text{ even} \end{array} \tag{17 a}$$

$$\begin{array}{l} A \leftrightarrow B_x,\ A \leftrightarrow B_y,\ B_x \leftrightarrow B_z,\ B_y \leftrightarrow B_z \\ \text{for } m' \neq 0, \text{ odd} \end{array} \tag{17 b}$$

$$\begin{array}{l} A \leftrightarrow A,\ B_x \leftrightarrow B_x,\ B_y \leftrightarrow B_y,\ B_z \leftrightarrow B_z \\ \text{for } m' = 0, l \text{ even} \end{array} \tag{17 c}$$

$$\begin{array}{l} A \leftrightarrow B_z,\ B_x \leftrightarrow B_y \\ \text{for } m' = 0, l \text{ odd}. \end{array} \tag{17 d}$$

Collisional selection rules in terms of the parity of K_-K_+ are obtained from (17) and Table 1 for a given representation of the principal axes a, b, c by x, y, z. The nonvanishing multipole moments $M_{lm'}$ are obtained by consideration of the configuration symmetry of the colliding molecules. In some cases of configuration symmetry [1] it is necessary to use instead of the $M_{lm'}$ linear combinations of them given by

$$M^{\pm}_{lm'} = \frac{1}{\sqrt{2}}\,(M_{lm'} \pm M_{l-m'}), \quad m' \neq 0 \tag{18}$$

which belong to irreducible representations of the molecular point group (see example of C_{2v}-symmetry below). To formulate collisional selection rules we then have to rewrite the interaction potential $V(t)$ (7) in terms of M_{l0} and $M^{\pm}_{lm'}$. By using (13) and (18) we have for $m' \neq 0$:

Table 2. Species relationship of functions $S^l_{m'm\varrho}$.

Species of $V(x, y, y)$	m'	$l+\varrho$
A	e	e
B_z	e	o
B_y	o	e
B_x	o	o

$$\begin{aligned} D^l_{m'm}(\alpha\beta\gamma)\,M_{lm'} + D^l_{-m'm}(\alpha\beta\gamma)\,M_{l-m'} \\ &= D^l_{m'm}(\alpha\beta\gamma)\cdot\frac{1}{\sqrt{2}}\,(M^+_{lm'} + M^-_{lm'}) + D^l_{-m'm}(\alpha\beta\gamma)\cdot\frac{1}{\sqrt{2}}\,(M^+_{lm'} - M^-_{lm'}) \\ &= \frac{1}{\sqrt{2}}\,[D^l_{m'm}(\alpha\beta\gamma) + D^l_{-m'm}(\alpha\beta\gamma)]\,M^+_{lm'} + \frac{1}{\sqrt{2}}\,[D^l_{m'm}(\alpha\beta\gamma) - D^l_{m'm}(\alpha\beta\gamma)]\,M^-_{lm'} \\ &= S^l_{m'm0}(\alpha\beta\gamma)\,M^+_{lm'} + S^l_{m'm0}(\alpha\beta\gamma)\,M^-_{lm'}\,. \end{aligned} \tag{19}$$

Inserting (19) for $m' \neq 0$ into (7) gives:

$$\begin{aligned} V(t) = 4\pi \sum_{l_1 l_2} \sum_{m_1 m_2} C_{l_1 l_2}\, C(l_1 l_2 l, m_1 m_2 \overline{m})\, &\frac{Y^*_{l\overline{m}}[\Theta(t), \Phi(t)]}{R(t)^{l+1}} \\ \times \{ S^{l_1}_{0m_1}(\alpha_1\beta_1\gamma_1)\,M_{l_1 0}\, &S^{l_2}_{0m_2}(\alpha_2\beta_2\gamma_2)\,M_{l_2 0} \\ &+ S^{l_1}_{0m_1}(\alpha_1\beta_1\gamma_1)\,M_{l_1 0} \sum_{m_2'>0} [S^{l_2}_{m_2' m_2 0}(\alpha_2\beta_2\gamma_2)\,M^+_{l_2 m_2'} + S^{l_2}_{m_2' m_2 1}(\alpha_2\beta_2\gamma_2)\,M^-_{l_2 m_2'}] \\ &+ S^{l_2}_{0m_2}(\alpha_2\beta_2\gamma_2)\,M_{l_2 0} \sum_{m_1'>0} [S^{l_1}_{m_1' m_1 0}(\alpha_1\beta_1\gamma_1)\,M^+_{l_1 m_1'} + S^{l_1}_{m_1' m_1 1}(\alpha_1\beta_1\gamma_1)\,M^-_{l_1 m_1'}] \\ &+ \sum_{\substack{m_1'>0 \\ m_2'>0}} [S^{l_1}_{m_1' m_1 0}(\alpha_1\beta_1\gamma_1)\,M^+_{l_1 m_1'} + S^{l_1}_{m_1' m_1 1}(\alpha_1\beta_1\gamma_1)\,M^-_{l_1 m_1'}] \\ &\times [S^{l_2}_{m_2' m_2 0}(\alpha_2\beta_2\gamma_2)\,M^+_{l_2 m_2'} + S^{l_2}_{m_2' m_2 1}(\alpha_2\beta_2\gamma_2)\,M^-_{l_2 m_2'}] \}\,. \end{aligned} \tag{20}$$

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* Product of species which belong to $|J^{\mathrm{i}}K^{\mathrm{i}}K^{\mathrm{i}}M^{\mathrm{i}}\rangle$, $|J^{\mathrm{f}}K^{\mathrm{f}}K^{\mathrm{f}}M^{\mathrm{f}}\rangle$ and $D^l_{m'm}(\alpha\beta\gamma)$.

As before we will only consider molecule 1 and omit the indices. For $m' \neq 0$ we then have to consider the matrix elements

$$\langle J^{\mathrm{i}} K_-{}^{\mathrm{i}} K_+{}^{\mathrm{i}} M^{\mathrm{i}} \,|\, S^{l}_{m'm0}(\alpha\beta\gamma) \,|\, J^{\mathrm{f}} K_-{}^{\mathrm{f}} K_+{}^{\mathrm{f}} M^{\mathrm{f}} \rangle \quad (21\,\mathrm{a})$$

for nonzero $\overset{+}{M}_{lm'}$ and

$$\langle J^{\mathrm{i}} K_-{}^{\mathrm{i}} K_+{}^{\mathrm{i}} M^{\mathrm{i}} \,|\, S^{l}_{m'm1}(\alpha\beta\gamma) \,|\, J^{\mathrm{f}} K_-{}^{\mathrm{f}} K_+{}^{\mathrm{f}} M^{\mathrm{f}} \rangle \quad (21\,\mathrm{b})$$

for nonzero $\overset{-}{M}_{lm'}$.

Examining Table 2 gives the collisional selection rules for $m' \neq 0$:

$$\begin{aligned}
&A \leftrightarrow A,\ B_x \leftrightarrow B_x,\ B_y \leftrightarrow B_y,\ B_z \leftrightarrow B_z\\
&\qquad \text{for } m' \text{ even} \quad l \text{ even},\ \overset{+}{M}_{lm'} \neq 0,\\
&\qquad\qquad\qquad\quad\ l \text{ odd},\ \overset{-}{M}_{lm'} \neq 0; \qquad (22\,\mathrm{a})\\
&A \leftrightarrow B_z,\ B_y \leftrightarrow B_x\\
&\qquad \text{for } m' \text{ even} \quad l \text{ odd},\ \overset{+}{M}_{lm'} \neq 0,\\
&\qquad\qquad\qquad\quad\ l \text{ even},\ \overset{-}{M}_{lm'} \neq 0; \qquad (22\,\mathrm{b})\\
&A \leftrightarrow B_y,\ B_x \leftrightarrow B_z\\
&\qquad \text{for } m' \text{ odd} \quad l \text{ even},\ \overset{+}{M}_{lm'} \neq 0,\\
&\qquad\qquad\qquad\quad\ l \text{ odd},\ \overset{-}{M}_{lm'} \neq 0; \qquad (22\,\mathrm{c})\\
&A \leftrightarrow B_x,\ B_y \leftrightarrow B_z\\
&\qquad \text{for } m' \text{ odd} \quad l \text{ odd},\ \overset{+}{M}_{lm'} \neq 0,\\
&\qquad\qquad\qquad\quad\ l \text{ even},\ \overset{-}{M}_{lm'} \neq 0. \qquad (22\,\mathrm{d})
\end{aligned}$$

For $m' = 0$, see (17 c, d).

It should be noted that the rules (17) and (22) hold partly also in the higher order approximation of the collisional process *. Thus, the rules (17a, c) and (22 a) hold irrespective of the order of perturbation treatment ** and rules (17 d), (22 b – d) have to be extended by (22 a).

In the case of (17b) no specific selection rules are obtained in higher order approximation.

Application of the Theory to an Example

In order to illustrate the preceding discussion, we will now consider the special case of colliding ethylene oxide, C_2H_4O, molecules. Collisional energy transfer between rotational levels of C_2H_4O and C_2D_4O has been extensively studied in our laboratory by means of four-level microwave-microwave double resonance technique [6, 19]. The results of this work will be published separately and give strong support for the theoretical arguments.

With the correlation

$$b, a, c \leftrightarrow z, y, x \qquad (23)$$

of the molecule fixed axes, the z-axis is chosen along the axis of maximum rotation symmetry. The molecular point group is C_{2v}, the character table of which is given in Table 3.

Table 3. Character Table of C_{2v}-group.

Species	Operations E	 $C_2{}^z$	 $\sigma(x, z)$	 $\sigma(y, z)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

We will now derive from symmetry considerations the nonvanishing permanent multipole moments of C_2H_4O up to $l = 2$, i. e. dipole and quadrupole moments. Higher order multipole moments are believed to be less important for weak collisions due to the decrease of range $[1/R(t)^{l+1}$ in (7)] with increasing l. The multipole moments $M_{lm'}$ are defined in polar coordinates r, Θ_0, Φ_0 of the molecular point charges according to (6). The polar coordinates transform under the operations of the C_{2v}-group like (Index j suppressed):

$$\begin{aligned}
E:&\ r \leftrightarrow r,\ \Theta_0 \leftrightarrow \Theta_0,\ \Phi_0 \leftrightarrow \Phi_0,\\
C_2{}^z:&\ r \leftrightarrow r,\ \Theta_0 \leftrightarrow \Theta_0,\ \Phi_0 \leftrightarrow \Phi_0 + \pi,\\
\sigma(y, z):&\ r \leftrightarrow r,\ \Theta_0 \leftrightarrow \Theta_0,\ \Phi_0 \leftrightarrow -\Phi_0 + 2\pi,\\
\sigma(y, z):&\ r \leftrightarrow r,\ \Theta_0 \leftrightarrow \Theta_0,\ \Phi_0 \leftrightarrow -\Phi_0 + \pi. \qquad (24)
\end{aligned}$$

With (6) and (24) and the symmetry behaviour of the spherical harmonics $Y_{lm'}(\Theta_0, \Phi_0)$ it follows that the $M_{lm'}$ induce reducible representations of C_{2v}, see Table 4.

By reduction we obtain the result that the $\overset{\pm}{M}_{lm'}$ as defined in (18) and M_{l0} transform according to

Table 4. Transformation properties of the $Y_{lm'}$ under C_{2v}.

	E	$C_2{}^z$	$\sigma(x, z)$	$\sigma(y, z)$
Y_{10}	1	1	1	1
$\begin{pmatrix} Y_{11} \\ Y_{1-1} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$
Y_{20}	1	1	1	1
$\begin{pmatrix} Y_{21} \\ Y_{2-1} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$
$\begin{pmatrix} Y_{22} \\ Y_{2-2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

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* Sor second order contributions see Ref. [7a] and Verter et al [18].

** Interference effects due to the presence of different multipole terms [7a] are not considered here.

irreducible representations of C_{2v}. The relation of the M_{l0} and $M^{\pm}_{lm'}$ to the species is given in Table 5.

Species of C_{2v}	
A_1	M_{10}, M_{20}, M^{+}_{22}
A_2	M^{-}_{22}
B_1	M^{+}_{11}, M^{+}_{21}
B_2	M^{-}_{11}, M^{-}_{21}

Table 5. Assignment of $M^{\pm}_{lm'}$, M_{l0} to species of C_{2v}-group.

Using the alternative definitions of the dipole and quadrupole moments with respect to the principal axes *a*, *b*, *c* we have:

$$\mu_g = \sum_j q_j g_j \tag{25 a}$$

$$Q_{gg'} = \sum_j q_j (3\, g_j g_j' - r_j^2\, \delta_{gg'}) \quad (g, g' = a, b, c) \tag{25 b}$$

where the sum is over all charges q_j with cartesian coordinates a_j, b_j, c_j. Then for ethylene oxide with axis representation (23):

$$M_{10} = \sqrt{\frac{3}{4\pi}}\,\mu_b\,, \tag{26 a}$$

$$M_{20} = \frac{1}{4}\sqrt{\frac{5}{\pi}}\,Q_{bb}\,,$$

$$M^{+}_{22} = \frac{1}{4}\sqrt{\frac{5}{3\pi}}\,(Q_{cc} - Q_{aa})\,. \tag{26 b}$$

First we consider the collisional selection rules which arise from the nonvanishing expectation value of the dipole moment μ_b. In first order we have with (10), (17 d), and (23):

$$\Delta J = J^{\mathrm{i}} - J^{\mathrm{f}} = 0, \pm 1 \qquad (0 \not\leftrightarrow 0) \tag{27a}$$

$$\Delta M = M^{\mathrm{i}} - M^{\mathrm{f}} = 0, \pm 1 \tag{27b}$$

$$A \leftrightarrow B_b\,, \quad B_c \leftrightarrow B_a\,. \tag{27 c}$$

With Table 1 we rewrite (27 c) in terms of the eveness or oddness of $K_- K_+$:

$$K_-{}^{\mathrm{i}} K_+{}^{\mathrm{i}} \leftrightarrow K_-{}^{\mathrm{f}} K_+{}^{\mathrm{f}}: \qquad \mathrm{ee} \leftrightarrow \mathrm{oo} \qquad \mathrm{oe} \leftrightarrow \mathrm{eo}\,. \tag{28 a}$$

In our approximation the following transitions are forbidden:

$$\begin{array}{ll} \mathrm{ee} \not\leftrightarrow \mathrm{ee} & \mathrm{ee} \not\leftrightarrow \mathrm{eo} \\ \mathrm{oo} \not\leftrightarrow \mathrm{oo} & \mathrm{ee} \not\leftrightarrow \mathrm{oe} \\ \mathrm{eo} \not\leftrightarrow \mathrm{eo} & \mathrm{oo} \not\leftrightarrow \mathrm{eo} \\ \mathrm{oe} \not\leftrightarrow \mathrm{oe} \quad (28\,\mathrm{b}) & \mathrm{oo} \not\leftrightarrow \mathrm{oe}\,. \quad (28\,\mathrm{c}) \end{array}$$

Note that rule (28) holds partly in higher order approximation, i. e. no dipole collision induced transitions of the type (28 c) occur.

The collisional selection rules due to the quadrupol moments M_{20} and M^{+}_{22} are given by (10), (17 c), (22 a) and (23) to

$$\Delta J = 0, \pm 1, \pm 2 \qquad (0 \not\leftrightarrow 0), \ (0 \not\leftrightarrow 1) \tag{29 a}$$

$$\Delta M = 0, \pm 1, \pm 2 \tag{29 b}$$

$$A \leftrightarrow A, \ B_a \leftrightarrow B_a \ \ B_b \leftrightarrow B_b\,, \ B_c \leftrightarrow B_c\,. \tag{29 c}$$

Rewriting (29 c) in terms of $K_- K_+$ gives:

$$K_-{}^{\mathrm{i}} K_+{}^{\mathrm{i}} \leftrightarrow K_-{}^{\mathrm{f}} K_+{}^{\mathrm{f}}: \qquad \begin{array}{l} \mathrm{ee} \leftrightarrow \mathrm{ee} \\ \mathrm{eo} \leftrightarrow \mathrm{eo} \\ \mathrm{oe} \leftrightarrow \mathrm{oe} \\ \mathrm{oo} \leftrightarrow \mathrm{oo}\,. \end{array} \tag{30}$$

Rule (30) is not restricted to the first order perturbation treatment.

Acknowledgements

We thank Dr. L. Engelbrecht for helpful discussions. The support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemie is gratefully acknowledged.

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