

COMMUTATION RELATIONS FOR THE ANGULAR MOMENTUM OPERATORS IN ETHANE-LIKE MOLECULES

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The Coriolis ζ -sum rules and the angular momentum commutators have been derived for ethane-like molecules. Commutation relations obtained for a completely free internal rotation have been compared with those obtained for a small barrier to internal rotation.

Watson^{1,2} has recently shown that the commutation relations for the operators of the so-called vibrational angular momentum, in nonlinear and linear rigid molecules, do not assume the simple form of the commutation relations for the operators of the molecule-fixed components of the total angular momentum. An extension of this treatment to molecules with internal rotation is not straightforward because of the presence of additional "internal" angular momenta in these molecules, *i.e.* the internal rotation angular momentum and the torsional vibrational angular momentum, and because of the general dependence of the Coriolis ζ -constants on the torsional variables.

In the present paper, Coriolis ζ -sum rules and commutation relations have been derived for the angular momentum operators for the ethane-like molecules with low barrier to internal rotation. Commutation relations obtained for completely free internal rotation have been compared with those obtained for a nonzero barrier to internal rotation.

The Vibrational-Rotational-Torsional Hamiltonian

An example of a molecule to which the following treatment can be applied is dimethylacetylene (Fig. 1). It is convenient to divide the molecule into a "top half" and "frame half": $(\text{CH}_3\text{C}_a-\text{C}_c\equiv)$ and $(\equiv\text{C}_d-\text{C}_b\text{CH}_3)$ and to introduce four coordinate systems: the space-fixed axis system XYZ ; the molecule-fixed axis system xyz ; the "top" axis system $x_t y_t z_t$; the "frame" axis system $x_f y_f z_f$ (Fig. 1). The orientation of the top axis system with respect to the space-fixed axis system is defined by the three Euler angles Θ , Φ , χ_t , and similarly of the frame axis system by the Euler angles Θ , Φ , χ_f . Instead of χ_t , χ_f the variables x and γ can be defined,

$$x = \frac{1}{2}(\chi_t + \chi_f), \quad \gamma = \frac{1}{2}(\chi_t - \chi_f). \quad (1a, b)$$

According to the formalism introduced by Hougen³, the moving systems of axes are defined by the following conditions (Eqs (3) ref.³)

$$\sum_i m_i \mathbf{S}_i^{-1}(0, 0, \pm\gamma) \cdot \mathbf{d}_i = 0, \quad (2a)$$

$$\sum_i m_i \mathbf{S}_i^{-1}(0, 0, \pm\gamma) [\mathbf{r}_i^0 \times \mathbf{d}_i] = \sum_i m_i [\mathbf{S}_i^{-1}(0, 0, \pm\gamma) \cdot \mathbf{r}_i^0] \times [\mathbf{S}_i^{-1}(0, 0, \pm\gamma) \cdot \mathbf{d}_i] = 0, \quad (2b)$$

$$\mathbf{k} \cdot \left[\sum_{i=f} m_i \mathbf{r}_i^0 \times \mathbf{d}_i \right] = 0. \quad (2c)$$

In Eqs (2), \sum_i represents a sum over all nuclei, $\sum_{i=f}$ represents a sum over the nuclei in the top minus the sum over the nuclei in the frame, \mathbf{k} is the unit vector along the z axis. The vectors \mathbf{r}_i ,

$$\mathbf{r}_i = \mathbf{r}_i^0 + \mathbf{d}_i \quad (3)$$

are the position vectors of the i -th "top" nucleus in the "top" axis system, and the position vectors of the "frame" nucleus in the "frame" axis system; \mathbf{r}_i^0 's represent the reference positions of the nuclei chosen so that all bond lengths and angles, except the torsional angle, have their equilibrium values; the \mathbf{d}_i represent vibrational displacements for the equilibrium positions of the "top" and "frame" nuclei in the corresponding "top" and "frame" axis systems. The matrix $\mathbf{S}_i^{-1}(0, 0, \pm\gamma)$ is defined as

$$\mathbf{S}_i^{-1}(0, 0, \pm\gamma) = \begin{bmatrix} \cos \gamma & \mp \sin \gamma & 0 \\ \pm \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (4)$$

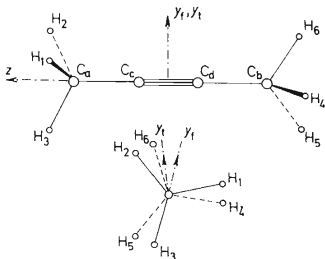


FIG. 1

The Rotor-Fixed Axes in Dimethylacetylene

where the upper sign holds for the nuclei in the top half, the lower sign for the nuclei in the frame half of the molecule. The variables describing the motions of the atomic nuclei are \mathbf{R}_0 , the Cartesian coordinates in the space-fixed axis system of the centre of mass of the molecule; the Euler angles Θ, Φ, χ ; the angle of internal rotation γ ; and the symmetry coordinates of vibration S_k ($k = 1, 2, \dots, 3N - 7$). The symmetry coordinates S_k as well as the non-genuine normal coordinates T_x, T_y, T_z corresponding to the translation (Eq. (2a)), R_x, R_y, R_z corresponding to the rotation (Eq. (2b)), and τ corresponding to the torsion (Eq. (2c)) are related by an orthonormal transformation to the vibrational displacements \mathbf{d}_i ,

$$\bar{S}_k = \sum_{\alpha, i} I_{\alpha i, k}^S(\gamma) [m_i^{1/2} d_{\alpha i}] \quad \begin{array}{l} k = 1, 2, \dots, 3N \\ i = 1, 2, \dots, N \\ \alpha = x, y, z \end{array} \quad (5)$$

where \bar{S}_k is a symmetry coordinate S_k or a non-genuine vibrational coordinate, $d_{\alpha i}$ is the α -th component of the vector \mathbf{d}_i in the "top" or "frame" system of axes. Some of the transformation coefficients $I_{\alpha i, k}^S$ pertaining to the symmetry coordinates S_k are certainly functions of the torsional angle³ γ .

The rotational variables Θ, Φ, χ , and γ and the coordinate \mathbf{R}_0 are related to the space-fixed Cartesian coordinates of the nuclei \mathbf{R}_i by the equation:

$$\mathbf{R}_i = \mathbf{R}_0 + \mathbf{S}^{-1}(\Theta, \Phi, \chi) \cdot \mathbf{S}_i^{-1}(0, 0, \pm\gamma) \cdot (\mathbf{r}_i^0 + \mathbf{d}_i), \quad (6)$$

where $\mathbf{S}(\Theta, \Phi, \chi)$ is the 3×3 transformation matrix given explicitly in Appendix I of ref.⁴. According to Eq. (6), the velocity $\dot{\mathbf{R}}_i$ of the nucleus with respect to the space-fixed axes XYZ is

$$\dot{\mathbf{R}}_i = \dot{\mathbf{R}}_0 + \dot{\mathbf{S}}^{-1}(\Theta, \Phi, \chi) \cdot \mathbf{t}_i + \mathbf{S}^{-1}(\Theta, \Phi, \chi) \cdot \dot{\mathbf{t}}_i, \quad (7)$$

where

$$\mathbf{t}_i = \mathbf{S}_i^{-1}(0, 0, \pm\gamma) \cdot (\mathbf{r}_i^0 + \mathbf{d}_i), \quad \dot{\mathbf{t}}_i = \dot{\mathbf{S}}_i^{-1}(0, 0, \pm\gamma) \cdot (\mathbf{r}_i^0 + \mathbf{d}_i) + \mathbf{S}_i^{-1}(0, 0, \pm\gamma) \cdot \dot{\mathbf{d}}_i. \quad (8)$$

In Eq. (8), the expression for $\dot{\mathbf{t}}_i$ was derived under the assumption that the reference positions of the atomic nuclei do not depend on the torsional angle γ , i.e., $(d/dt) r_{x_i}^0 = (d/dt) r_{y_i}^0 = (d/dt) r_{z_i}^0 = 0$.

By use of Eqs (7), (8), and (2), the kinetic energy of vibration, rotation and torsion then can be written in the form,

$$2T (\equiv \sum_i m_i \dot{\mathbf{R}}_i \cdot \dot{\mathbf{R}}_i) = \sum_{\alpha, \beta} I_{\alpha\beta} \omega_\alpha \omega_\beta + \dot{\gamma}^2 I_{zz} + \sum_i m_i \dot{\mathbf{d}}_i \cdot \dot{\mathbf{d}}_i + 2\omega \cdot \sum_i m_i \mathbf{S}_i^{-1}(0, 0, \pm\gamma) \cdot (\mathbf{d}_i \times \dot{\mathbf{d}}_i) + 2\dot{\gamma} \left[\sum_{i-f} m_i (\mathbf{d}_i \times \dot{\mathbf{d}}_i)_z \right] + 2\dot{\gamma} \sum_{\alpha} \omega_\alpha I_{\alpha z}, \quad (9)$$

where ω_α are the components of the angular velocity vector with respect to the molecule-fixed axes,

$$I_{\alpha\alpha} = \sum_i m_i (t_{\beta i}^2 + t_{\gamma i}^2), \quad (\alpha, \beta, \gamma = x, y, z), \quad (10a)$$

$$I_{\alpha\beta} = -\sum_i m_i t_{\alpha i} t_{\beta i} \quad (\alpha \neq \beta), \quad (10b)$$

$$I_{xz} = -\sum_{i=f} m_i t_{xi} t_{zi}, \quad I_{yz} = -\sum_{i=f} m_i t_{yi} t_{zi}, \quad I_{zz} = \sum_{i=f} m_i (t_{xi}^2 + t_{yi}^2). \quad (11)$$

The definition of the normal coordinates of vibration which have to be introduced into Eq. (9) requires some discussion. Let \mathbf{d} be the column matrix of the coordinates $m_i^{1/2} d_{\alpha i}$ ($\alpha = x, y, z; i = 1, 2, \dots, N$), and \mathbf{Q} the column matrix of the normal coordinates of vibration Q_k (including the non-genuine normal coordinates defined by Eqs (2)).

Then

$$\mathbf{d} = \mathbf{L}(\gamma) \mathbf{Q}, \quad (12)$$

where $\mathbf{L}(\gamma)$ is a $3N \times 3N$ orthogonal matrix of the coefficients $l_{\alpha i, k}(\gamma)$ which are in general functions of the torsional angle γ .

Therefore

$$\dot{\mathbf{d}} = \dot{\gamma} \mathbf{L}' \mathbf{Q} + \mathbf{L} \dot{\mathbf{Q}}, \quad (13)$$

where the elements of the matrix \mathbf{L}' are $l'_{\alpha i, k} = d/d\gamma(l_{\alpha i, k})$.

Hence

$$\sum_i m_i \dot{\mathbf{d}}_i \cdot \dot{\mathbf{d}}_i = \ddot{\mathbf{d}} \cdot \dot{\mathbf{d}} = \ddot{\mathbf{Q}} \dot{\mathbf{Q}} + \dot{\gamma} (\ddot{\mathbf{Q}} \tilde{\mathbf{L}} \mathbf{L}' \mathbf{Q} + \tilde{\mathbf{Q}} \tilde{\mathbf{L}}' \mathbf{L} \dot{\mathbf{Q}}) + \dot{\gamma}^2 \tilde{\mathbf{Q}} \tilde{\mathbf{L}}' \mathbf{L}' \mathbf{Q}. \quad (14)$$

The matrix $\tilde{\mathbf{L}} \mathbf{L}'$ is an antisymmetric matrix since $\tilde{\mathbf{L}} \mathbf{L} = \mathbf{E}_{3N}$ and from the orthogonality of the transformation (12), $d/d\gamma(\tilde{\mathbf{L}} \mathbf{L}) = \tilde{\mathbf{L}}' \mathbf{L} + \tilde{\mathbf{L}} \mathbf{L}' = 0$, therefore $\tilde{\mathbf{L}} \mathbf{L}' = -\tilde{\mathbf{L}}' \mathbf{L}$.

Hence

$$\tilde{\mathbf{Q}} \tilde{\mathbf{L}} \mathbf{L}' \mathbf{Q} = \sum_{kl} \zeta'_{kl} Q_k \dot{Q}_l, \quad (15a)$$

where

$$\zeta'_{kl} = \sum_{\alpha, i} l_{\alpha i, l} l'_{\alpha i, k} \quad (16)$$

$\zeta'_{kl} = -\zeta'_{lk}$. $\tilde{\mathbf{Q}} \tilde{\mathbf{L}} \mathbf{L}' \mathbf{Q}$ is referred to as a Coriolis coupling term. Since similarly

$$\tilde{\mathbf{Q}} \tilde{\mathbf{L}}' \mathbf{L} \dot{\mathbf{Q}} = \sum_{kl} \zeta'_{lk} Q_k \dot{Q}_l \quad (15b)$$

then

$$\tilde{\mathbf{Q}} \tilde{\mathbf{L}} \mathbf{L}' \mathbf{Q} + \tilde{\mathbf{Q}} \tilde{\mathbf{L}}' \mathbf{L} \dot{\mathbf{Q}} = 2 \sum_{kl} \zeta'_{kl} Q_k \dot{Q}_l. \quad (17)$$

The last term on the right side of Eq. (14) is

$$\dot{\gamma}^2 \tilde{Q} \tilde{L}' \mathbf{L}' \mathbf{Q} = \dot{\gamma}^2 \sum_{kl} k'_{kl} Q_k Q_l, \quad (18)$$

where

$$k'_{kl} = \sum_{\alpha, i} l'_{\alpha i, k} l'_{\alpha i, l} \quad (19)$$

$k'_{kl} = +k'_{lk}$. $\tilde{Q} \tilde{L}' \mathbf{L}' \mathbf{Q}$ is a contribution to the potential energy term.

Consider now the potential energy V of the molecule as a function of the vibrational displacements \mathbf{d}_i and the angle of internal rotation γ . Expanding V in terms of \mathbf{d}_i (taken at the reference configuration) gives

$$V = V_0(\gamma) + \sum_{\alpha, i} (\partial V / \partial d_{\alpha i})_0 d_{\alpha i} + \frac{1}{2} \sum_{\alpha, \beta, i, j} (\partial^2 V / \partial d_{\alpha i} \partial d_{\beta j})_0 d_{\alpha i} d_{\beta j} + \text{higher terms}. \quad (20)$$

In Eq. (20), $V_0(\gamma)$ depends only on the torsional angle γ and therefore represents the potential energy of internal rotation of the non-vibrating molecule. The second term on the right side of Eq. (20) vanishes since, for the reference configuration which was chosen, the pure vibrational energy has a minimum and hence all the linear force constants $(\partial V / \partial d_{\alpha i})_0 = 0$. In general the quadratic force constants $F_{\alpha i, \beta j} = (\partial^2 V / \partial d_{\alpha i} \partial d_{\beta j})_0$ have to be considered as functions³ of γ . The quadratic term can be written as

$$\sum_{\alpha, \beta, i, j} F_{\alpha i, \beta j} d_{\alpha i} d_{\beta j} = \sum_{\alpha, \beta, i, j} F_{\alpha i, \beta j}^0 d_{\alpha i} d_{\beta j} + \sum_{\alpha, \beta, i, j} F_{\alpha i, \beta j}^{(\gamma)} d_{\alpha i} d_{\beta j}, \quad (21)$$

where $F_{\alpha i, \beta j}^0$ is that part of the force constant $F_{\alpha i, \beta j}$ which is γ -independent.

In the treatment described above, equation (14) was the result of the mere requirement that $\mathbf{L}(\gamma)$ is an orthogonal matrix with coefficients which are in general functions of γ . Further requirement which specifies that Eq. (12) is a transformation to the normal coordinates of vibration is that the quadratic part of the potential energy expansion is diagonal in the \mathbf{Q} , *i.e.*

$$V = V_0(\gamma) + \frac{1}{2} \sum_{k=1}^{3N-7} \lambda_k Q_k^2, \quad (22)$$

where the λ_k are in general functions of γ . However, it is possible to define normal coordinates of vibration in terms of which only the γ -independent part of the quadratic term is diagonal in \mathbf{Q} ,

$$V = V_0(\gamma) + \frac{1}{2} \sum_k \lambda_k^0 Q_k^2 + \sum_{kl} F_{kl}(\gamma) Q_k Q_l \quad (23)$$

and to consider the third term on the right side of Eq. (23) as the vibrational contribution to the potential energy of internal rotation. In other words, the normal co-

ordinates may be obtained through a transformation $\mathbf{L}(\gamma)$ (Eq. (12)), where the columns of $\mathbf{L}(\gamma)$ are the eigenvectors of the vibrational secular equation with force constants which are either γ -dependent or γ -independent. The latter definition may be convenient when the barrier to internal rotation is small and the vibrational contribution to the barrier of internal rotation may be considered as a small perturbation⁵. The following treatment will be based on the definition of the normal coordinates obtained from the γ -dependent force constants and the results will be then compared with the results obtained from the γ -independent force constants. Using Eqs. (13) and (14), equation (9) can be written as

$$2T = \sum_{\alpha, \beta} I_{\alpha\beta} \omega_{\alpha} \omega_{\beta} + \dot{\gamma}^2 I_{zz} + \sum_{k=1}^{3N-7} \dot{Q}_k^2 + 2 \sum_{\alpha} \omega_{\alpha} (\sum_{kl} \zeta_{kl}^{\alpha} Q_k \dot{Q}_l + \dot{\gamma} \sum_{kl} \eta_{kl}^{\alpha} Q_k Q_l) + 2\dot{\gamma} [\sum_{kl} \zeta_{kl}^{\gamma} Q_k \dot{Q}_l + \dot{\gamma} \sum_{kl} \bar{\eta}_{kl}^{\gamma} Q_k Q_l + \sum_{\alpha} \omega_{\alpha} I_{\alpha z}], \quad (24)$$

where the Coriolis coupling coefficients are defined as*

$$\zeta_{kl}^{\alpha} = \sum_{\beta\delta} e_{\alpha\beta\delta} \sum_i I_{\beta i, k}^t I_{\delta i, l}^t \quad (25a)$$

$$\bar{\zeta}_{kl}^{\alpha} = \sum_{\beta\delta} e_{\alpha\beta\delta} \sum_{i=f} I_{\beta i, k}^t I_{\delta i, l}^t, \quad \zeta_{kl}^{\gamma} = \bar{\zeta}_{kl}^{\gamma} + \zeta_{kl}^{\gamma'} \quad (25b, c)$$

The $I_{\alpha i, k}^t$ in Eqs (25) are defined as

$$I_{\alpha i, k}^t = \sum_{\beta=x, y, z} \mathbf{S}_i^{-1}(0, 0, \pm\gamma)_{\alpha\beta} I_{\beta i, k} \quad (26)$$

The quantities η_{kl}^{α} , $\bar{\eta}_{kl}^{\gamma}$ in Eq. (24) are defined as

$$\eta_{kl}^{\alpha} = \sum_{\beta\delta} e_{\alpha\beta\delta} \sum_i I_{\beta i, k}^t I_{\delta i, l}^t, \quad \bar{\eta}_{kl}^{\alpha} = \sum_{\beta\delta} e_{\alpha\beta\delta} \sum_{i=f} I_{\beta i, k}^t I_{\delta i, l}^t, \quad (27, 28)$$

$$\bar{\eta}_{kl}^{\gamma} = \bar{\eta}_{kl}^{\gamma} + \frac{1}{2} k'_{kl} \quad (29)$$

In Eqs (27)–(29) the $I_{\alpha i, k}^t$ are defined as

$$I_{\alpha i, k}^t = \sum_{\beta} \mathbf{S}_i^{-1}(0, 0, \pm\gamma)_{\alpha\beta} I'_{\beta i, k} \quad (30)$$

Eq (24) can be rewritten into the momentum form,

$$2T = \sum_{\alpha\beta} \mu_{\alpha\beta} (\mathbf{\Pi}_{\alpha} - \pi_{\alpha}) (\mathbf{\Pi}_{\beta} - \pi_{\beta}) + \sum_k P_k^2 \quad (31)$$

* In the following equations the unit antisymmetric tensor $e_{\alpha\beta\delta}$ is used as $e_{xyz} = e_{yzx} = e_{zxy} = 1$, $e_{xzy} = e_{yxz} = e_{zyx} = -1$, and $e_{\alpha\beta\delta} = 0$ if any pair α, β, δ , are identical.

where now $\bar{\alpha}, \bar{\beta} = x, y, z$ or γ . In Eq. (29), Π_α ($\alpha = x, y, z$) are the molecule-fixed components of the total angular momentum,

$$\Pi_\alpha \left(\equiv \frac{\partial T}{\partial \omega_\alpha} \right) = \sum_{\beta} I_{\alpha\beta} \omega_\beta + \sum_{kl} \zeta_{kl}^\alpha Q_k \dot{Q}_l + \dot{\gamma} \left(\sum_{kl} \eta_{kl}^\alpha Q_k Q_l + I_{\alpha z} \right); \quad (32)$$

the momentum conjugate to γ is

$$\Pi_\gamma \left(\equiv \frac{\partial T}{\partial \dot{\gamma}} \right) = I_{zz} \dot{\gamma} + \sum_{kl} \zeta_{kl}^\gamma Q_k \dot{Q}_l + 2\dot{\gamma} \sum_{kl} \bar{\eta}_{kl}^\gamma Q_k Q_l + \sum_{\alpha=x,y,z} \omega_\alpha I_{\alpha z} + \sum_\alpha \omega_\alpha \sum_{kl} \eta_{kl}^\alpha Q_k Q_l; \quad (33)$$

the momentum conjugate to Q_l is

$$P_l \left(\equiv \frac{\partial T}{\partial \dot{Q}_l} \right) = \dot{Q}_l + \sum_\alpha \omega_\alpha \sum_k \zeta_{kl}^\alpha Q_k + \dot{\gamma} \sum_k \zeta_{kl}^\gamma Q_k; \quad (34)$$

the so-called vibrational angular momentum (Footnote 1 in ref.¹) π_α is defined as

$$\pi_\alpha = \sum_{kl} \zeta_{kl}^\alpha Q_k P_l; \quad \alpha = x, y, z \quad (35)$$

the so-called vibrational torsional angular momentum π_γ is defined as

$$\pi_\gamma = \sum_{kl} \zeta_{kl}^\gamma Q_k P_l. \quad (36)$$

The quantities $\mu_{\alpha\beta}$ in Eq. (31) are complicated functions of the geometry of the molecule and of the normal coordinates of vibration; their explicit form can be found in ref.³.

Orthogonality Conditions of the Coefficients of the Coordinate Transformation

The orthogonality of the transformation (12) implies a number of relations among the coefficients $l_{\alpha i, k}$. Since the coefficients $l_{\alpha i, k}^t$ defined by Eq. (26) appear in the expressions, rather than the coefficients $l_{\alpha i, k}$ (defined by Eqs (12)), relations will be given here in terms of the coefficients $l_{\alpha i, k}^t$. The orthogonality conditions which follow from the sum over the atoms are:

$$\sum_{\alpha, i} l_{\alpha i, k}^t l_{\alpha i, l}^t = \sum_{\alpha, i} l_{\alpha i, k} l_{\alpha i, l} = \delta_{kl}, \quad (37)$$

$$\sum_i m_i^{1/2} l_{\alpha i, k}^t = 0, \quad (38)$$

$$\sum_{\beta, \delta} e_{\alpha\beta\delta} \sum_i m_i^{1/2} l_{\beta i, \delta}^t l_{\alpha i, k}^t = 0, \quad (39)$$

$$\sum_{t-f} m_i^{1/2} \sum_{\beta, \delta} e_{z\beta\delta} t_{\beta i}^0 l_{\delta i, k}^t = \sum_{t-f} m_i^{1/2} \sum_{\beta, \delta} e_{z\beta\delta} r_{\beta i}^0 l_{\delta i, k}^t, \quad (40)$$

where $t_{\alpha i}^0$ ($\alpha = x, y, z$) are the molecule-fixed components of the vector \mathbf{t}_i for $\mathbf{d}_i = 0$ (Eq. (8)). The orthogonality conditions which follow from the sum over all the normal coordinates are:

$$\sum_{k=1}^{3N-7} l_{\alpha i, k}^t l_{\beta j, k}^t = \delta_{ij} \delta_{\alpha\beta} - m_i^{1/2} m_j^{1/2} M^{-1} \delta_{\alpha\beta} - \\ - \sum_{\epsilon, \kappa, \delta} e_{\alpha\kappa\epsilon} e_{\beta\delta\epsilon} (I_{\epsilon\epsilon}^0)^{-1} m_i^{1/2} m_j^{1/2} t_{\kappa i}^0 t_{\delta j}^0 + (-1)^{\delta_{ij}} \sum_{\kappa, \delta} e_{\alpha\kappa\epsilon} e_{\beta\delta\epsilon} (I_{zz}^0)^{-1} m_i^{1/2} m_j^{1/2} t_{\kappa i}^0 t_{\delta j}^0, \quad (41)$$

where $M = \sum_i m_i$, $I_{\epsilon\epsilon}^0$ is the value of the quantity $I_{\epsilon\epsilon}$ for all $\mathbf{d}_i = 0$ (Eqs (10a) and (8)), and $\delta_{ij} = 1$ when i and j simultaneously refer either to the top or to the frame nuclei and $\delta_{ij} = 0$ otherwise. Note that Eq. (41) holds for an orientation of the molecule-fixed axes and the axis of the inertia ellipsoid such that the equilibrium products of inertia vanish (Eq. (14) in ref.¹ where this simplification was not considered deliberately).

Interaction Coefficients and Sum Rules

We define the coefficients $a_k^{\alpha\beta}$ and $\bar{a}_k^{\alpha\beta}$ as the derivatives of $I_{\alpha\beta}$ and $\bar{I}_{\alpha\beta}$ along Q_k at the reference configuration:

$$\left(\frac{\partial I_{\alpha\beta}}{\partial Q_k} \right)_0 = a_k^{\alpha\beta}, \quad \left(\frac{\partial \bar{I}_{\alpha\beta}}{\partial Q_k} \right)_0 = \bar{a}_k^{\alpha\beta}. \quad (42a, b)$$

It is then obvious from the definition of $I_{\alpha\beta}$ (Eqs (10)) and of $\bar{I}_{\alpha\beta}$ (Eqs (11)) that

$$a_k^{\alpha\beta} = a_k^{\beta\alpha} = 2 \sum_{x, \delta, \epsilon} e_{\alpha x \epsilon} e_{\beta \delta \epsilon} \sum_i m_i^{1/2} t_{x i}^0 l_{\delta i, k}^t, \quad (43)$$

and

$$\bar{a}_k^{\alpha\beta} = \bar{a}_k^{\beta\alpha} = 2 \sum_{x, \delta, \epsilon} e_{\alpha x \epsilon} e_{\beta \delta \epsilon} \sum_{t-f} m_i^{1/2} t_{x i}^0 l_{\delta i, k}^t. \quad (43b)$$

The following sum rules can be then derived for the Coriolis coupling coefficients from Eqs (25a), (41), and (43)

$$\sum_m \zeta_{km}^{\alpha\beta} \zeta_{lm}^{\beta\alpha} = \delta_{\alpha\beta} \delta_{kl} - \sum_i l_{\beta i, k}^t l_{\alpha i, l}^t - \frac{1}{4} \sum_{\epsilon} a_k^{\alpha\epsilon} (I_{\epsilon\epsilon}^0)^{-1} a_l^{\epsilon\beta} - \frac{1}{4} \bar{a}_k^{\alpha\epsilon} (I_{zz}^0)^{-1} \bar{a}_l^{\epsilon\beta}. \quad (44)$$

The derivation of the sum rule $\sum_m \zeta_{km}^{\alpha\beta} \zeta_{lm}^{\gamma\alpha}$ ($\alpha = x, y, z$) requires a preliminary discussion of the Coriolis coupling coefficient ζ_{lm}^{α} defined by Eq. (25c) as the sum of $\bar{\zeta}_{lm}^{\alpha}$ and ζ_{lm}^{α} . The Coriolis coupling term ζ_{kl}^{α} has been defined in Eq. (16) in terms of the $l_{\alpha i, k}^t$; however it is desirable to express ζ_{kl}^{α} in terms of the coefficients $l_{\alpha i, k}^t$. With the use of Eqs (16), (26), and (30) one obtains after some algebraic manipulation

$$\zeta_{ki}^{\gamma'} = \zeta_{ik}^z + \sum_{\alpha,i} l_{\alpha i, i}^t (l_{\alpha i, k}^t)' , \quad (45)$$

where

$$(l_{\alpha i, k}^t)' = \partial / \partial \gamma (l_{\alpha i, k}^t) .$$

Hence

$$\zeta_{ki}^{\gamma} = \zeta_{ki}^z + \zeta_{ik}^z + \sum_{\alpha,i} l_{\alpha i, i}^t (l_{\alpha i, k}^t)' = \sum_{\alpha,i} l_{\alpha i, i}^t (l_{\alpha i, k}^t)' , \quad (46)$$

and

$$\sum_m \zeta_{km}^{\alpha} \zeta_{lm}^{\gamma} = \eta_{ki}^{*\alpha} - \frac{1}{4} \sum_{c=x,y,z} a_k^{\alpha c} (I_{cc}^0)^{-1} \bar{a}_i^{cz} - \frac{1}{4} \bar{a}_k^{\alpha z} (I_{zz}^0)^{-1} a_i^{zz} , \quad (47)$$

where

$$\eta_{ki}^{*\alpha} = \sum_{\beta\delta} e_{\alpha\beta\delta} \sum_i l_{\beta i, k}^t (l_{\delta i, i}^t)' ; \quad (48)$$

Eq. (47) has been obtained with the use of Eqs (46), (41), and of the relations $\partial / \partial \gamma (a_k^{\alpha\beta}) = \partial / \partial \gamma (a_k^{\beta\alpha})$ and $\partial / \partial \gamma (\bar{a}_k^{\alpha\beta}) = \partial / \partial \gamma (\bar{a}_k^{\beta\alpha})$.

Commutation Relations For the Angular Momentum Operators

The operators of the components of the total angular momentum with respect to the molecule-fixed axis system xyz (Eq. (32)) satisfy the same commutation relations as in rigid molecules:*

$$[\Pi_{\alpha}, \Pi_{\beta}] = \Pi_{\alpha} \Pi_{\beta} - \Pi_{\beta} \Pi_{\alpha} = -i\hbar \sum_{\delta} e_{\alpha\beta\delta} \Pi_{\delta} . \quad (49)$$

Π_{α} ($\alpha = x, y, z$) commutes with the operator of the torsional angular momentum Π_{γ} (Eq. (33))

$$[\Pi_{\alpha}, \Pi_{\gamma}] = 0 \quad (50)$$

and with the operators of the components of the vibrational angular momentum π_{α} ($\alpha = x, y, z$) (Eq. (35)) and of the vibrational torsional angular momentum π_{γ} (Eq. (36)),

$$[\Pi_{\alpha}, \pi_{\beta}] = 0, \quad [\Pi_{\alpha}, \pi_{\gamma}] = 0 \quad (51, 52)$$

because the corresponding operators act on different coordinates.

Commutators of the "internal" angular momenta are much more complicated than the commutators discussed above. Consider first the commutation relations for the operators of the components of the vibrational angular momentum (including the vibrational torsional angular momentum). The general definition of these operators is (Eqs (35) and (36))

$$\pi_{\bar{\alpha}} = \sum_{kl} \zeta_{kl}^{\bar{\alpha}} Q_k P_l, \quad \bar{\alpha} = x, y, z \quad \text{or} \quad \gamma \quad (53)$$

* These relations are obtained when the operators Π_{α} ($\alpha = x, y, z$) are expressed in terms of the operators conjugate to the rotational variables Θ, Φ, x Eqs. (6) in Sect. 11-4 of ref. (4).

so that the use of the commutation relations between the Q 's and P 's gives

$$[\pi_{\bar{\alpha}}, \pi_{\bar{\beta}}] = i\hbar \sum_{k,l,m} (\zeta_{km}^{\bar{\alpha}} \zeta_{lm}^{\bar{\beta}} - \zeta_{km}^{\bar{\beta}} \zeta_{lm}^{\bar{\alpha}}) Q_k P_l, \quad \bar{\alpha} = x, y, z \quad \text{or} \quad \gamma. \quad (54)$$

The sum rule (44) then gives the following commutation relations for the operators of the components of the vibrational angular momenta π_x, π_y, π_z :

$$\begin{aligned} [\pi_{\alpha}, \pi_{\beta}] &= i\hbar \sum_{\delta=x,y,z} e_{\alpha\beta\delta} \pi_{\delta} - \frac{i\hbar}{4} \sum_{kl} \sum_{\delta} a_k^{\alpha\delta} (I_{\delta\delta}^0)^{-1} a_l^{\delta\beta} (Q_k P_l - Q_l P_k) - \\ &- \frac{i\hbar}{4} \sum_{kl} \bar{a}_k^{\alpha z} (I_{zz}^0)^{-1} \bar{a}_l^{\beta z} (Q_k P_l - Q_l P_k). \end{aligned} \quad (55)$$

Consider now the commutation relations between π_{α} ($\alpha = x, y, z$) and π_{γ} . The sum rule (47) gives in this case the following commutation relations:

$$\begin{aligned} [\pi_{\alpha}, \pi_{\gamma}] &= i\hbar \sum_{kl} (\eta_{kl}^{*\alpha} - \eta_{lk}^{*\alpha}) Q_k P_l - \frac{i\hbar}{4} \sum_{kl} \sum_{\epsilon=x,y,z} a_k^{\alpha\epsilon} (I_{\epsilon\epsilon}^0)^{-1} \bar{a}_l^{\epsilon\gamma} (Q_k P_l - Q_l P_k) - \\ &- \frac{i\hbar}{4} \sum_{kl} \bar{a}_k^{\alpha z} (I_{zz}^0)^{-1} a_l^{\gamma z} (Q_k P_l - Q_l P_k). \end{aligned} \quad (56)$$

Consider finally the commutators of the torsional angular momentum operator Π_{γ} with the vibrational angular momentum π_{α} ($\alpha = x, y, z$) and the vibrational torsional angular momentum π_{γ} . The Coriolis coupling terms ζ_{kl}^{α} ($\alpha = x, y, z$) (Eq. (25a)) must be considered in general as the functions of the torsional angle^{5,6} γ . Hence from the definition of ζ_{kl}^{α} one obtains:

$$\frac{\partial \zeta_{kl}^{\alpha}}{\partial \gamma} = \sum_{\beta} e_{\beta\alpha z} \zeta_{kl}^{\beta} + (\eta_{kl}^{\alpha} - \eta_{lk}^{\alpha}) \quad (57)$$

and the commutator of the torsional angular momentum Π_{γ} with the vibrational angular momentum π_{α} ($\alpha = x, y, z$) then becomes

$$[\Pi_{\gamma}, \pi_{\alpha}] = \sum_{\beta=x,y,z} e_{\alpha\beta z} \pi_{\beta}^{\text{tr}} - i\hbar \sum_{kl} (\eta_{kl}^{\alpha} - \eta_{lk}^{\alpha}) Q_k P_l \quad \alpha = x, y, z, \quad (58)$$

where

$$\pi_{\alpha}^{\text{tr}} = \sum_{kl} \zeta_{kl}^{\alpha} Q_k P_l, \quad \alpha = x, y, z. \quad (59)$$

For the case of the commutator $[\Pi_{\gamma}, \pi_{\gamma}]$, I was not able to find an expression for the derivative

$$\frac{\partial \zeta_{kl}^{\gamma}}{\partial \gamma} = \sum_{\alpha, i} (l_{\alpha i, i}^{\alpha})' (l_{\alpha i, k}^{\alpha}) + \sum_{\alpha, i} (l_{\alpha i, i}^{\alpha}) (l_{\alpha i, k}^{\alpha})'' \quad (60)$$

in terms of the quantities introduced in this paper. Because the Coriolis constant ζ_{kl}^{γ} is γ -independent if the γ -independent force constant matrix is introduced (Eq. (23)), no further attempt was made to express $\partial \zeta_{kl}^{\gamma} / \partial \gamma$ in terms of some newly defined quantities (see also Eq. (62)).

DISCUSSION

Commutation relations for the "internal" angular momenta, derived in this paper, assume a more complicated form than the commutation relations for "rigid" molecules. Some of these commutators can be simplified when the γ -independent force constant matrix is used in the normal coordinate calculation (Eq. (23) and the following paragraph). In this case, the Coriolis constants ζ_{kl}^x and ζ_{kl}^y remain γ -dependent but the Coriolis constants ζ_{kl}^z and ζ_{kl}^{γ} become γ -independent⁵. Then

$$[\Pi_{\gamma}, \pi_z] = 0, \quad \text{and} \quad [\Pi_{\gamma}, \pi_{\gamma}] = 0. \quad (61, 62)$$

An interesting problem is whether it would be possible or not to simplify the vibrational-rotational-torsional Hamiltonian using the sum rules and commutation relations derived in this paper, in a way similar to that found by Watson for "rigid" molecules^{1,2}. The form of the sum rules and of the commutation relations found in this paper for ethane-like molecules indicates that such simplification might be possible. A preliminary analysis however revealed that the amount of algebraic work required in such a treatment would be considerable and the problem has not yet been studied in detail.

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