Short Communication

A Matrix Formalism for Raman Optical Activity (ROA) as Applied to Intensity Sum Rules

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Raman optical activity (ROA) is a spectroscopic technique[1-3] which can provide information about chiral molecules. Various sum rules for the ROA intensities have been derived by Cuony and Hug,[4] and by Polavarapu.[5,6] The purpose of this communication is to show that the relationships involved in these sum rules can be conveniently expressed in terms of a matrix formalism for ROA presented by Rupprecht in Ref. 7. Since this reference is not easily accessible, not occurring in a regular journal, a short summary of the basic approach will be given (Ref. 7 is available from the author on request).

In this matrix formalism the anisotropic parts of the electric and magnetic dipole polarizability tensors α and β, respectively, and of the tensor, δ, related to the electric quadrupole polarizability tensor A through $\delta_{ij} = \Sigma \varepsilon_{ikl} A_{klj}$, are expressed as 6×1 column vectors. The order of the components has been chosen as in the Mayants-Averbukh Raman intensity theory,[8] and these column vectors are denoted with an overbar [eqns. (1a,b) and (1c)].

$$
\bar{\alpha}_{\text{aniso}} = \begin{bmatrix} \alpha_{1,\text{aniso}} \\ \vdots \\ \vdots \\ \alpha_{\vartheta,\text{aniso}} \\ \vdots \\ \alpha_{6,\text{aniso}} \end{bmatrix} = \begin{bmatrix} (\alpha_{xx}-a) \\ \alpha_{xy} \\ \alpha_{xz} \\ (\alpha_{yy}-a) \\ \alpha_{yz} \\ (\alpha_{zz}-a) \end{bmatrix}
\tag{1a}
$$

$$
\bar{\beta}_{\text{aniso}} = \begin{bmatrix} (\beta_{xx}-b) \\ \frac{1}{2}(\beta_{xy}+\beta_{yx}) \\ \frac{1}{2}(\beta_{xz}+\beta_{zx}) \\ (\beta_{yy}-b) \\ \frac{1}{2}(\beta_{yz}+\beta_{zy}) \\ (\beta_{zz}-b) \end{bmatrix}
\tag{1b}
$$

$$
\bar{\delta}_{\text{aniso}} = \begin{bmatrix} A_{yzx}-A_{zyx} \\ \frac{1}{2}(A_{yzy}-A_{zyy}+A_{zxx}-A_{xzx}) \\ \frac{1}{2}(A_{yzz}-A_{zyz}+A_{xyx}-A_{yxx}) \\ A_{zxy}-A_{xzy} \\ \frac{1}{2}(A_{zxz}-A_{xzz}+A_{xyy}-A_{yxy}) \\ A_{xyz}-A_{yxz} \end{bmatrix}
\tag{1c}
$$

The mean values $a = (1/3)\text{Tr}\alpha$ and $b = (1/3)\text{Tr}\beta$ in eqns. (1a,b) are treated separately as scalars (δ is traceless since A is symmetric in the last two indices).

The derivatives of these quantities with respect to the tth normal vibrational coordinate Q_t (evaluated for the equilibrium configuration of the molecule) occur in the tensor invariants[5,7] γ_t^2, β_t^2, δ_t^2, a_t and b_t as illustrated for β_t^2 in Ref. 9 (see Ref. 7 for the other invariants). These derivatives may be evaluated in terms of derivatives with respect to the Cartesian atomic displacement vectors $\bar{X}^{(a)}$, i.e. in terms of atomic polar tensors (APT's) $(\partial \bar{\alpha}_{\text{aniso}}/\partial \bar{X}^{(a)})$ and atomic axial tensors (AAT's) $(\partial \bar{\beta}_{\text{aniso}}/\partial \bar{X}^{(a)})$ and $(\partial \bar{\delta}_{\text{aniso}}/\partial \bar{X}^{(a)})$ as illustrated in eqns. (7) and (8) of Ref. 9.

As an illustration of the application of this formalism, let us consider the frequency-weighted sum rule recently presented by Polavarapu.[6] This relates the ROA intensities of fundamental transitions of isotopic molecules and is useful for determining force constants. In the present matrix formalism, eqn. (1) of Ref. 6 can be written as

$$
\sum_t \beta_t^2/4\pi^2 c^2 \nu_t^2 =
$$

$$
\frac{3}{2} \sum_{j,k} \left(\frac{\partial \widetilde{\bar{\alpha}}_{\text{aniso}}}{\partial R_j} \right) \mathbf{K} \left(\frac{\partial \bar{\beta}_{\text{aniso}}}{\partial R_k} \right) F_{jk}^{-1}
\tag{2}
$$

where ν_t is the frequency (in cm^{-1}) of vibration t, R_j is the jth internal coordinate and F_{jk}^{-1} an element of the inverse force constant matrix in internal coordinates. $\mathbf{K} = \text{diag}(1,2,2,1,2,1)$, and $\sim$ signifies the transpose.

As an additional example, the anisotropic parts provided by eqn. (4) of Ref. 6 can be written as

$$
\left(\frac{\partial \bar{\beta}_{\text{aniso}}}{\partial R_j} \right)_2 = \left(\frac{\partial \bar{\beta}_{\text{aniso}}}{\partial R_j} \right)_1 + \sum_a \left(\frac{\partial \bar{\beta}_{\text{aniso}}}{\partial \bar{\varrho}} \right)_1 \beta_{a1}(\mathbf{A}_{aj})_2
\tag{3}
$$

where $\bar{\varrho} = (T_x T_y T_z R_x R_y R_z)$ represents the six normal rotranslational coordinates (see also Ref. 10). The indices a, 1 and 2 refer to atom a and to two isotopic molecules. Thus, β_a and $\mathbf{A}_a$ are submatrices pertaining to atom a of β and $\mathbf{A}$, respectively (not to be confused with the magnetic dipole

and electric quadrupole polarizability tensors), defined in Ref. 6 (see also Ref. 10). The last symbol in eqn. (3) signifies the jth column of $\mathbf{A}_{a2}$. The analogous equation for the mean value b is obtained by replacing $\bar{\beta}_{aniso}$ with b.

The great usefulness of this matrix formalism in the present context is, however, to be found in the uniform evaluation of the derivatives with respect to the normal rotranslational coordinates ϱ in terms of matrices. Referring to Ref. 7 the result is:

$$\left(\frac{\partial\bar{\alpha}_{aniso}}{\partial\varrho}\right) = \left[\mathbf{0}_{6\times3} \middle| [[\alpha_{aniso}]]\,\mathbf{I}^{-\frac{1}{2}}\right] \tag{4a}$$

$$\left(\frac{\partial\bar{\beta}_{aniso}}{\partial\varrho}\right) = \left[-\frac{1}{4c}\,[[\alpha_{aniso}]]\,m^{-\frac{1}{2}} \middle| [[\beta_{aniso}]]\,\mathbf{I}^{-\frac{1}{2}}\right] \tag{4b}$$

$$\left(\frac{\partial\bar{\delta}_{aniso}}{\partial\varrho}\right) = \left[-\frac{3}{4}\,[[\alpha_{aniso}]]\,m^{-\frac{1}{2}} \middle| [[\delta_{aniso}]]\,\mathbf{I}^{-\frac{1}{2}}\right] \tag{4c}$$

$$\left(\frac{\partial a}{\partial\varrho}\right) = \left(\frac{\partial b}{\partial\varrho}\right) = \left[\mathbf{0}_{1\times3} \middle| \mathbf{0}_{1\times3}\right] = \mathbf{0}_{1\times6} \tag{4d}$$

where m is the mass of the molecule and $\mathbf{I}$ the moment of inertia tensor. $\mathbf{0}_{k\times l}$ is a $k\times l$ zero matrix, and $[[\alpha_{aniso}]]$ is the following 6×3 matrix:

$$[[\alpha_{aniso}]] = \begin{bmatrix} 0 & 2\alpha_{3,a} & -2\alpha_{2,a} \\ -\alpha_{3,a} & \alpha_{5,a} & (\alpha_{1,a}-\alpha_{4,a}) \\ \alpha_{2,a} & (\alpha_{6,a}-\alpha_{1,a}) & -\alpha_{5,a} \\ -2\alpha_{5,a} & 0 & 2\alpha_{2,a} \\ (\alpha_{4,a}-\alpha_{6,a}) & -\alpha_{2,a} & \alpha_{3,a} \\ 2\alpha_{5,a} & -2\alpha_{3,a} & 0 \end{bmatrix} \tag{5}$$

where $\alpha_{\theta,a} \equiv \alpha_{\theta,aniso}$ [eqn. (1a)].

This quantity concerns the equilibrium configuration of the molecule. $[[\beta_{aniso}]]$ and $[[\delta_{aniso}]]$ are completely analogous, i.e. $\alpha_{\theta,aniso}$ in eqn. (5) is replaced by $\beta_{\theta,aniso}$ and $\delta_{\theta,aniso}$, respectively, from eqns. (1b) and (1c). It has been shown[11] that $[[\alpha_{aniso}]]$ represents α_{aniso} expressed as a third-rank axial tensor which is symmetric in the first two indices. However, $[[\beta_{aniso}]]$ and $[[\delta_{aniso}]]$ are polar tensors.[7]

If the matrix products $(\partial\bar{\beta}_{aniso}/\partial\varrho)\beta_a$ [occurring in eqn. (3)] and $(\partial\bar{\delta}_{aniso}/\partial\varrho)\beta_a$ are evaluated in the principal axis coordinate system, using the expressions above and the explicit form of the 6×3 matrix β_a displayed e.g. in Table 2 of Ref. 12, then the result is found to be equivalent to the expressions given by Polavarapu in Table 1 of Ref. 6 (a misprint occurs in the third column of that table: the sign of $y_A A_{yxx}/I_x$ should be $+$). However, it should be pointed out that the a vector of Ref. 6 represents a tensor with non-zero trace, while the corresponding vector of the present work

$\bar{\delta}_{aniso}$, eqn. (1c), represents the traceless tensor. As a result the $\bar{a}$ vector requires knowledge of more diagonal tensor components than are actually needed, and this uneconomical property is also transferred to the derivatives of a with respect to ϱ occurring in Table 1 of Ref. 6.

In our view, the present matrix formalism is not only more economical but also more uniform and transparent than the partial matrix formalism introduced by Polavarapu[6] in terms of the column vectors a and b. The reason for this is that the column vectors in eqn. (1) are all defined in the same way as the anisotropic parts of the molecular tensors, providing a minimal set of components, and that they are introduced from the beginning and are used throughout. As a result the derivatives in eqn. (4) will all be expressed in terms of the matrices $[[\;]]$ defined in eqn. (5). This uniformity should make the formalism suitable for computer calculations.

The other intensity sum rules in ROA[4,5] can also be expressed conveniently with this matrix formalism, as illustrated in Ref. 7. Among other things it was shown[7] that the APT's and AAT's can be divided into atomic vibration, rotation and translation tensors which add up to the vibrational, rotational and translational contributions, respectively, in the sum rule equations. The great usefulness of symmetry invariant APT's and AAT's, referred to their respective atomic coordinate systems, is also demonstrated in Ref. 7 in connection with sum rules, by analogy with the treatment in Ref. 13. This illustrates further the usefulness of this matrix formalism for theoretical developments in ROA.

References

1. Barron, L. D. *Molecular Light Scattering and Optical Activity*, Cambridge University Press, Cambridge 1982.
2. Barron, L. D. and Vrbancich, J. *Topics Curr. Chem. 123* (1984) 151.
3. Polavarapu, P. L. In: Durig, J. R., Ed., *Vibrational Spectra and Structure*, Elsevier, New York 1984, Vol. 13.
4. Cuony, B. and Hug, W. *Chem. Phys. Lett. 84* (1981) 131.
5. Polavarapu, P. L. *Chem. Phys. Lett. 123* (1986) 545.
6. Polavarapu, P. L. *Chem. Phys. Lett. 139* (1987) 558.
7. Rupprecht, A. *A Matrix Formalism for Raman Optical Activity (ROA) Inspired by the Mayants-Averbukh and the Polar Tensor Intensity Theories. Chem. Commun. Univ. Stockholm 6* (1987).
8. Mayants, L. S. and Averbukh, B. S. *J. Mol. Spectrosc. 22* (1967) 197.
9. Rupprecht, A. *Mol. Phys. 63* (1988) 951.
10. Rupprecht, A. *J. Mol. Spectrosc. 89* (1981) 356.
11. Rupprecht, A. *J. Mol. Spectrosc. 108* (1984) 165.
12. Person, W. B. and Newton, J. H. *J. Chem. Phys. 61* (1974) 1040.
13. Rupprecht, A. *Mol. Phys. 63* (1988) 955.