Remark on the Off-Diagonal Rotational g-Tensor Elements in Asymmetric-Top Molecules

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The isotopic dependence of the **g**-tensor of an asymmetric top molecule is investigated. A relationship is proposed which may be used to determine the **g**-tensor for isotopic species without measurements.

In the study of molecular properties, one has to deal with various tensorial quantities [1]. Their behaviour under an isotopic substitution can sometimes give valuable information, when the assumption is made that the electronic distribution remains unchanged. A very well known example is that of the moment of inertia tensor **I** whose behaviour under isotopic substitution is related to the geometry of the molecule by Kraitchman's equations [2], or the nuclear quadrupole coupling tensor eqQ which allows to "measure" the electric field gradient at the quadrupolar nucleus, and thereby gives information on the charge distribution [3]. The magnetic susceptibility tensor $\boldsymbol{\chi}$ or the spin-rotation tensor **C** are other examples which have been studied recently [4].

The **g**-tensor has also been studied, first by Schwarz [5]. But these studies have generally been limited to the case where inertial axes are subject to a simple translation between parent and daughter molecule. In this case the electric dipole moment $\boldsymbol{\mu}$ is often parallel to an axis of inertia, and the isotopic substitution which preserves the molecular symmetry may be used to determine the sign of $\boldsymbol{\mu}$ [6]. But when a rotation of axis is also present some other information can be gained. For instance the relative sign of g_{xx} and g_{yy} can be determined if the rotation mixes these components. The object of the present note is to show that the non-diagonal elements of **g** can be obtained when an isotopic substitution induces a rotation of axes. Once all the elements of **g** are known for the parent species, they could be predicted for all the isotopic species without measurements. The most interesting application is certainly for an accurate structure determination where it is necessary to correct the inertial tensor of each isotopic species for the electronic effects [6].

The expression of **g** is derived in [6–9], together with that of $\boldsymbol{\chi}^{\mathrm{p}}$ and $\boldsymbol{\chi}^{\mathrm{d}}$:

$$\boldsymbol{\chi}^{\mathrm{d}} = -e^2/(4c^2m)\,\langle 0|\sum (r_i^2\,\mathbb{1} - \boldsymbol{r}_i \otimes \boldsymbol{r}_i)\,|0\rangle, \tag{1}$$

$$\boldsymbol{\chi}^{\mathrm{p}} = -e^2/(2c^2m^2)\sum \langle 0|\,\boldsymbol{L}\,|k\rangle \otimes \langle k|\,\boldsymbol{L}\,|0\rangle/(E_0 - E_k), \tag{2}$$

where $\boldsymbol{L}$ is the total angular momentum of electrons, $|k\rangle$ the electronic wavefunctions, and E_k the corresponding energies. $\boldsymbol{r}_i$ defines the position of the ith electron, and the summation is taken over all electrons in the molecule.

$$\boldsymbol{\chi} = \boldsymbol{\chi}^{\mathrm{d}} + \boldsymbol{\chi}^{\mathrm{p}}, \tag{3}$$

$$\mathbf{g} = \mathbf{g}_{\mathrm{n}} + \mathbf{g}_{\mathrm{e}} \tag{4}$$

with

$$\mathbf{g}_{\mathrm{n}} = M_{\mathrm{p}} \sum Z_\alpha (r_\alpha^2\,\mathbb{1} - \boldsymbol{r}_\alpha \otimes \boldsymbol{r}_\alpha) \cdot \mathbf{I}^{-1}, \tag{5}$$

$$\mathbf{g}_{\mathrm{e}} = (2M_{\mathrm{p}}/m) \sum \langle 0|\,\boldsymbol{L}\,|k\rangle \otimes \langle k|\,\boldsymbol{L}\,|0\rangle \cdot \mathbf{I}^{-1}/(E_0 - E_k), \tag{6}$$

where $\boldsymbol{r}_\alpha$ defines the position of the αth nucleus. So that

$$\mathbf{g} \cdot \mathbf{I} = M_{\mathrm{p}} \{\sum Z_\alpha (r_\alpha^2\,\mathbb{1} - \boldsymbol{r}_\alpha \otimes \boldsymbol{r}_\alpha) + 2/m \sum \langle 0|\,\boldsymbol{L}\,|k\rangle \otimes \langle k|\,\boldsymbol{L}\,|0\rangle/(E_0 - E_k)\}. \tag{7}$$

At this stage we must stress the fact that **g** is in general not symmetric, although $\mathbf{g} \cdot \mathbf{I}$ is. Following Van Vleck [8] we remark that $\boldsymbol{\chi} = \boldsymbol{\chi}^{\mathrm{d}} + \boldsymbol{\chi}^{\mathrm{p}}$ is invariant to isotopic substitution and therefore the second sum of (7) behaves like

$$-\langle 0|\sum (r_i^2\,\mathbb{1} - \boldsymbol{r}_i \otimes \boldsymbol{r}_i)\,|0\rangle$$

for an isotopc substitution. That is:

$$\begin{aligned}\mathbf{g}' \cdot \mathbf{I}' - \mathbf{g} \cdot \mathbf{I} = M_{\mathrm{p}} \{&\sum Z_\alpha (r_\alpha'^2\,\mathbb{1} - \boldsymbol{r}_\alpha' \otimes \boldsymbol{r}_\alpha') \\ &- \langle 0|\sum (r_i'^2\,\mathbb{1} - \boldsymbol{r}_i' \otimes \boldsymbol{r}_i')\,|0\rangle \\ &- \sum Z_\alpha (r_\alpha^2\,\mathbb{1} - \boldsymbol{r}_\alpha \otimes \boldsymbol{r}_\alpha) \\ &+ \langle 0|\sum (r_i^2\,\mathbb{1} - \boldsymbol{r}_i \otimes \boldsymbol{r}_i)\,|0\rangle\},\end{aligned} \tag{8}$$

where the ′ (tick) stands for the isotopic species. Assuming that the electronic wavefunctions remain

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unchanged for an isotopic substitution and using

$$\Delta \boldsymbol{G} = \boldsymbol{r}_\alpha - \boldsymbol{r}'_\alpha = \boldsymbol{r}_i - \boldsymbol{r}'_i , \tag{9}$$

$$\boldsymbol{\mu} \;\; = e \left\{ \sum Z_\alpha \boldsymbol{r}_\alpha - \sum \boldsymbol{r}_i \right\} \tag{10}$$

we obtain

$$\mathbf{g}' \cdot \mathbf{I}' - \mathbf{g} \cdot \mathbf{I} \tag{11}$$

$$= M_\mathrm{p}/e \left\{ \Delta \boldsymbol{G} \otimes \boldsymbol{\mu} + \boldsymbol{\mu} \otimes \Delta \boldsymbol{G} - 2 (\boldsymbol{\mu} \cdot \Delta \boldsymbol{G}) \, \mathbb{1} \right\} .$$

Here $\Delta \boldsymbol{G}$ is the shift of the center of gravity by the isotopic substitution.

Using (11) to determine the dipole moment $\boldsymbol{\mu}$ is usually difficult because $\mathbf{g} \cdot \mathbf{I}$ and $\mathbf{g}' \cdot \mathbf{I}'$ are usually large terms whereas their difference is only about a tenth of them or even less. $\mathbf{g}$ has indeed to be very accurate for both isotopic species. Moreover rotation-vibration interaction effects may be non negligible [10]. If off-diagonal terms of $\mathbf{g}$ are to be determined, the rotation of inertial axes between parent and daughter must be big enough. On the other hand, the relative sign of g_{xx} and g_{yy} and the sign of $\boldsymbol{\mu}$ are much easier to determine.

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