On the Sign of the Off-Diagonal Elements of the Nuclear Quadrupole Coupling Tensor

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If off-diagonal elements of the nuclear quadrupole coupling tensor are determined from the rotational spectrum of only one isotopomer, the magnitude of the off-diagonal elements and the sign of the product $\chi_{ab}\chi_{bc}\chi_{ac}$ can be obtained but not the individual signs of the off-diagonal elements. In this article we give two proofs for this fact. A determination of the individual signs of the off-diagonal elements is only possible by analysing the spectra of more isotopomers.

Introduction

In the course of our work on van der Waals complexes containing a nucleus with a quadrupole moment resulting in a hyperfine structure in the microwave spectra we noticed a problem in the determinability of the sign of the off-diagonal elements of the quadrupole coupling tensor. Since only recently off-diagonal tensor elements of nuclei with small quadrupole moments could be determined directly due to the improved resolution and accuracy of the Fourier transform microwave (FTMW) spectroscopy, no detailed considerations about the sign of the off-diagonal elements are found in the standard literature [1].

In the first place we will proof that for three non-zero off-diagonal elements only the sign of the product $\chi_{ab}\chi_{bc}\chi_{ac}$: $\Sigma = \mathrm{sign}(\chi_{ab}\chi_{bc}\chi_{ac})$ can be determined from the experimental data of one isotopomer. The indices a, b, and c denote the intertial axes. The magnitude of χ_{gf}, $g, f = a, b, c$, and $g \neq f$ can also be determined, whereas for the sign of the individual elements χ_{gf} different choices exist constrained by Σ. This fact is consistent with the results given in [2]. For *n*-propyle iodide Fujitake and Hayashi could only determine Σ but not the individual signs of the three non-zero off-diagonal elements of the iodine coupling tensor. The authors obtained this result numerically by choosing different signs for their coupling elements when predicting energy levels by their computer progam.

After the general proof we will derive special cases.

Theory

The Hamiltonian [3] may be considered to consist of three parts:

$$H = H_r + H_{cd} + H_q, \tag{1}$$

where H_r is the rigid rotor-, H_{cd} the centrifugal distortion-, and H_q the quadrupole coupling-contribution. We assume the corresponding Hamiltonian matrix being set up in the basis $\langle J, K, I, F, M_F|$, where for the rotational part the symmetric rotor basis $\langle J, K|$ with the quantisation axis z in the molecule fixed principal axis system x, y, z is used. We further adopt the phase convention of Condon and Shortley [4]. The matrix elements of H_r and H_{cd} are real and diagonal in all quantum numbers except K. The matrix elements of H_q are given in [5], and in more detail in [6]. It should be mentioned that the coupling tensor χ is defined with respect to the geometry and charge distribution of the molecule and refers to the inertial axes a, b, c.

The diagonal coupling constants χ_{gg}, $g = a, b, c$, contribute to real diagonal and off-diagonal matrix elements. χ_{ab} is connected with real off-diagonal matrix elements and χ_{bc} and χ_{ac} with purely imaginary off-diagonal elements if the x, y, z axes with z being the quantisation axis are assigned to the a, b, c axes according to the representation I^r [7]. For the representation II^r χ_{bc} and for III^r χ_{ac} contribute to real and the other χ_{gf}, $g \neq f$ to purely imaginary off-diagonal matrix elements.

The real and diagonal matrix Λ of the energy eigenvalues is obtained from H by the transformation

$$X^{-1} H X = \Lambda, \tag{2}$$

where X is the diagonalising matrix. Taking the complex conjugate of (2) results in the same Λ. The complex conjugate of H can be obtained by changing the sign of the two purely imaginary coupling matrix elements. The choices which are possible for the sign χ_{gf}, $g \neq f$ and Σ with identical eigenvalues are shown in Table 1. It may be stated that choice 1 and 2 and in the same

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Table 1[a]. Choices of sign (χ_{gf}) and of $\Sigma = \mathrm{sign}\,(\chi_{ab}\,\chi_{bc}\,\chi_{ac})$ according to representation I^r.

Choice	sign χ_{ab}	sign χ_{bc}	sign χ_{ac}	Σ
1	+	+	+	+
2	+	−	−	+
3	−	−	+	+
4	−	+	−	+
5	−	−	−	−
6	−	+	+	−
7	+	+	−	−
8	+	−	+	−

[a] Choices with identical eigenvalues are separated by two horizontal lines.

Table 2. Transformation of the quadrupole coupling tensor elements under certain operations changing the positive direction of the principal inertial axes

χ_{gf}	Operation			
	$a \to -a$ $b \to -b$ $c \to -c$	$a \to -a$ $b \to -b$ or $c \to -c$	$c \to -c$ $a \to -a$ or $b \to -b$	$b \to -b$ $c \to -c$ or $a \to -a$
$\chi_{aa}, \chi_{bb}, \chi_{cc}$	1	1	1	1
χ_{ab}	1	1	−1	−1
χ_{bc}	1	−1	−1	1
χ_{ac}	1	−1	1	−1
$\chi_{ab}\,\chi_{bc}\,\chi_{ac}$	1	1	1	1

way 5 and 6 result in identical eigenvalues. By choosing the representation II^r and III^r it may be shown that the choices 1, 2, 3, 4 and 5, 6, 7, 8 result in identical eigenvalues, respectively. Thus the analysis of the spectrum provides only the magnitude of the off-diagonal elements of the coupling tensor and the sign of the product $\chi_{ab}\,\chi_{bc}\,\chi_{ac}$.

The case of two non-zero off-diagonal elements does not exist for symmetry reasons. If only one element is non-zero it may be expressed with purely imaginary matrix elements. From the considerations given above it follows that the sign χ_{gf}, $g \neq f$ is undetermined.

The problem may be considered from another point of view. The coupling tensor elements χ_{gf}, $g \neq f$ or $g = f$ are proportional to the second derivative of the potential V at the site of the coupling nucleus:

$$\chi_{gf} \sim \frac{\partial V^2}{\partial g\,\partial f}\,. \tag{3}$$

As the choice of the *positive direction* of the principal axes is free, the χ_{gf} transform according to Table 2 under the operations given. Under all operations the sign Σ does not change although the signs of the single tensor elements do. Therefore only the sign of Σ is determined.

It is possible to determine the sign of an off-diagonal element by isotopic substitution of a nucleus which is not the coupling one. This substitution does not change the eigenvalues of the quadrupole coupling tensor. A change in the elements is due to a rotation of the inertia principal axes system. If the structure of the molecule is given, it is possible to calculate off-diagonal elements by transformation of the diagonal elements of the quadrupole coupling tensor from the inertial axes system of one isotopomer into those of the other isotopomeres [8].

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