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Isotopic relations for tetrahedral and octahedral molecules.

(This paper is dedicated to the memory of Dr. Jon T. Hougen.)

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Abstract

The study and analysis of heavy spherical-top molecules is often not straightforward. The presence of hot bands and of many isotopologues can lead to a high line congestion very difficult for assignment. In this work, using a low-order model we have derived very simple isotopic relations in order to determine initial parameters of the analysis. We also show that an identical approach can be used for XY_4 and XY_6 molecules and all these results are illustrated by the comparison of numerical computations and experiments.

Keywords:

Spherical-top molecules, infrared absorption, isotopic relations

1. Introduction

Spherical-top molecules constitute an important class of molecular species whose study requires extensive use of symmetry [1] and group theory methods [2–4]. Besides the iconic example of methane [5], there exist many heavier species of this type, either tetrahedral like CF_4 [6], SiH_4 [7, 8], GeH_4 [9, 10], OsO_4 [11, 12], RuO_4 [13], P_4 [14], $C_{10}H_{16}$ [15], $C_6N_4H_{12}$ [16], ... or octahedral like SF_6 [17], SeF_6 [18], WF_6 [19], UF_6 [20], C_8H_8 [21], ... Most of them possess, in natural abundance, several isotopologues, some being sometimes quite rare [22] or even radioactive [13]. It is thus desirable to derive at least approximate relations to calculate isotopic shift relations for the lower order molecular parameters in order to get a first estimate and simulation of the absorption spectrum of low-abundance or radioactive isotopologues [9, 10, 13, 23].

Isotopic relations, however, have never been published in detail for such molecules, although there exist some partial studies [24–26] (some studies are part of old French theses which are difficult to find). In the present paper, we reinvestigate this question using a simple low-order model which is sufficient for the above-described purpose, that is to estimate initial parameters to allow initial simulations of infrared-active bands of minor isotopologues, based on the main isotopologue results. This method is applicable to all isotopologues with the same symmetry. The problem is more more complicated when the isotopic substitution lowers the symmetry (for instance, the passage from CH_4 to CH_2D_2). In the latter case, there exist other techniques, see for instance the work of Ulenikov *et al.* [27].

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20 Quadratic isotopic relations, for all molecules, are usually established using the GF matrix method [24], since force constants are invariant through isotopic substitution (within the Born-Oppenheimer approximation).

Here, we apply this method to infrared absorption active triply degenerate modes of tetrahedral and octahedral species using the approach of Hoy *et al.* [28]. This one leads, *a priori*, to two systems of linear equations that allow to calculate harmonic frequencies (or wavenumbers) and Coriolis constants for the different isotopologues.

We also propose an alternative approach based on force constants in the Cartesian coordinate system [29].

Section 2 describes the internal coordinate approach, while Section 3 presents the Cartesian coordinate point of view that leads to the isotopic relations derived in Section 4. Finally, we illustrate this through simple examples for tetrahedral and octahedral molecules in Sections 5 and 6, respectively.

2. XY_4 force constants in symmetrized internal coordinates

Let's consider a molecule made up of one nucleus X of mass M and four nuclei Y of mass m (see Figure 1). The symmetry group is the T_d group and the molecule possesses four vibration modes; $s = 1$ of symmetry A_1 , $s = 2$ of symmetry E and $s = 3, 4$ of symmetry F_2 . The quadratic potential, restricted to the modes 3 and 4, is expressed as:

$$V_{34} = \frac{1}{2} \sum_{\alpha=x,y,z} (F_{33} {}^i S_{3\alpha}^2 + F_{44} {}^i S_{4\alpha}^2 + 2F_{34} {}^i S_{3\alpha} {}^i S_{4\alpha}), \quad (1)$$

where the oriented symmetrized coordinates ${}^i S_{s\alpha}^2$ are expressed as a function of internal coordinates (see equations 2).

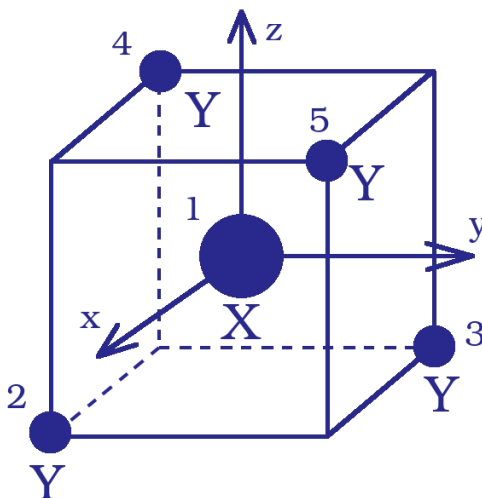


Figure 1: An XY_4 molecule in its reference configuration.

$$\begin{aligned}
iS_{3x} &= \frac{1}{2} (\Delta r_2 - \Delta r_3 - \Delta r_4 + \Delta r_5), \\
iS_{3y} &= \frac{1}{2} (-\Delta r_2 + \Delta r_3 - \Delta r_4 + \Delta r_5), \\
iS_{3z} &= \frac{1}{2} (-\Delta r_2 - \Delta r_3 + \Delta r_4 + \Delta r_5), \\
iS_{4x} &= \frac{1}{\sqrt{2}} r_e (\Delta \Theta_{34} - \Delta \Theta_{25}), \\
iS_{4y} &= \frac{1}{\sqrt{2}} r_e (\Delta \Theta_{24} - \Delta \Theta_{35}), \\
iS_{4z} &= \frac{1}{\sqrt{2}} r_e (\Delta \Theta_{23} - \Delta \Theta_{45}).
\end{aligned} \tag{2}$$

40 To determine force constants F_{33} , F_{34} and F_{44} , we use the GF method of Wilson [24] which allows to link these constants to the molecular masses and harmonic frequencies ω_s following the secular equation:

$$\det((GF)_{ij} - \lambda \delta_{ij}) = 0, \tag{3}$$

with

$$\lambda_s = 4\pi^2 c^2 \omega_s^2. \tag{4}$$

For F_2 type vibrations we obtain:

$$\lambda^2 - \lambda(F_{33}G_{33} + 2F_{34}G_{34} + F_{44}G_{44}) + \begin{vmatrix} F_{33} & F_{34} \\ F_{43} & F_{44} \end{vmatrix} \begin{vmatrix} G_{33} & G_{34} \\ G_{43} & G_{44} \end{vmatrix}, \tag{5}$$

45 where (F) and (G) are symmetric matrices and (G) depends of the choice of the symmetrized coordinates. The solutions are λ_3 and λ_4 with the following relations:

$$G_{33}F_{33} + G_{44}F_{44} + 2G_{34}F_{34} = \lambda_3 + \lambda_4, \tag{6}$$

$$(G_{33}G_{44} - G_{34}^2)(F_{33}F_{44} - F_{34}^2) = \lambda_3\lambda_4. \tag{7}$$

A third equation is needed to determine the three force constants. We use here this equation from Ref. [28]:

$$C_{33}F_{33} + C_{44}F_{44} + 2C_{34}F_{34} = \lambda_3\zeta_3 + \lambda_4\zeta_4, \tag{8}$$

50 where C is a matrix only depending of masses and geometry of the molecule and where Coriolis constants ζ_3 and ζ_4 are not independant and follow sum rules.

Nevertheless, the above equation (7) is not linear. So, by combining equations (6), (7) and (8), Hoy *et al.* [28] have obtained a third linear equation:

$$\begin{aligned}
&(G_{33}C_{34} - G_{33}C_{33})F_{33} + (G_{34}C_{44} - G_{44}C_{34})F_{44} + \\
&(G_{33}C_{44} - G_{44}C_{33})F_{34} = \epsilon(\lambda_3 - \lambda_4)\sqrt{\zeta_3\zeta_4|G| - |C|}, \tag{9}
\end{aligned}$$

where $|G|$ and $|C|$ stand for the G and C matrix determinants and $\epsilon = \pm 1$, leading to two possible solutions.

For XY_4 molecules, the G matrix has been given by Simanouti [30] and Aboumajd [26], while the C matrix was given by Mills [31]. Considering our choice of symmetrized coordinates, these matrices can be expressed as follows:

$$G = \begin{pmatrix} \frac{4}{3M} + \frac{1}{m} & \frac{8}{3M} \\ \frac{8}{3M} & \frac{16}{3M} + \frac{2}{m} \end{pmatrix}, C = \begin{pmatrix} \frac{4}{3M} & \frac{8}{3M} + \frac{1}{m} \\ \frac{8}{3M} + \frac{1}{m} & \frac{16}{3M} + \frac{1}{m} \end{pmatrix}. \quad (10)$$

Therefore (see Appendix 1), equation (9) leads to

$$\begin{aligned} F_{33} - 2F_{44} + F_{34} &= \mu m D \\ &= \epsilon (\lambda_3 - \lambda_4) \sqrt{2\mu M (1 - \zeta_4) \left(\frac{1}{2} + \zeta_4 \right)}. \end{aligned} \quad (11)$$

Then, we obtain force constants F_{33} , F_{44} and F_{34} by solving the system of 3 linear equations (6), (8) and (11). Their expressions are given in equations (12) and we have two solutions depending of the value of ϵ :

$$\begin{aligned} 6F_{33} &= (\mu + 2m) (\lambda_3 + \lambda_4) + \frac{1}{3} \left[(2m - \mu) (4\zeta_4 - 1) + 8\epsilon \sqrt{2\mu m (1 - \zeta_4) \left(\frac{1}{2} + \zeta_4 \right)} \right] (\lambda_3 - \lambda_4), \\ 6F_{34} &= (\mu - m) (\lambda_3 + \lambda_4) + \frac{1}{3} \left[(m + \mu) (1 - 4\zeta_4) + 2\epsilon \sqrt{2\mu m (1 - \zeta_4) \left(\frac{1}{2} + \zeta_4 \right)} \right] (\lambda_3 - \lambda_4), \\ 6F_{44} &= \left(\mu + \frac{m}{2} \right) (\lambda_3 + \lambda_4) + \frac{1}{3} \left[\left(\frac{m}{2} - \mu \right) (4\zeta_4 - 1) - 4\epsilon \sqrt{2\mu m (1 - \zeta_4) \left(\frac{1}{2} + \zeta_4 \right)} \right] (\lambda_3 - \lambda_4). \end{aligned} \quad (12)$$

Knowing numerical values of these constants from λ_3 , λ_4 and ζ_4 of one isotopologue, we can compute λ'_3 , λ'_4 and ζ'_4 for other isotopologues by using equations (5) and (8) and by adapting the G and C matrices.

3. Force constants of XY_4 in the symmetrized Cartesian coordinate system

In a symmetrized Cartesian coordinate system, the quadratic potential, restricted to modes $s = 3$ and $s = 4$, is expressed as [29]:

$$V_{34} = \frac{1}{2} \sum_{\alpha=x,y,z} (k_{33}^c S_{3\alpha}^2 + k_{44}^c S_{4\alpha}^2 + 2k_{34}^c S_{3\alpha}^c S_{4\alpha}), \quad (13)$$

where oriented symmetrized coordinates ${}^cS_{3\alpha}^2$ are expressed as a function of Cartesian coordinates:

$$\begin{aligned} {}^cS_{3\alpha} &= \frac{1}{4\sqrt{\mu m}} \left(m \sum_{i=2}^5 \alpha_i - M\alpha_1 \right), \\ {}^cS_{4x} &= \frac{1}{2\sqrt{2}} (-y_2 - y_3 + y_4 + y_5 - z_2 + z_3 - z_4 + z_5), \\ {}^cS_{4y} &= \frac{1}{2\sqrt{2}} (-x_2 - x_3 + x_4 + x_5 + z_2 - z_3 - z_4 + z_5), \\ {}^cS_{4z} &= \frac{1}{2\sqrt{2}} (y_2 - y_3 - y_4 + y_5 - x_2 + x_3 - x_4 + x_5). \end{aligned} \quad (14)$$

The λ 's are solutions of the secular equation:

$$\det(k_{ij} - m\lambda\delta_{ij}) = 0. \quad (15)$$

70 At that point, let $k_{33} = k_1$, $k_{44} = k_2$ and $k_{34} = k_3$ in order to simplify the notations. We thus write:

$$(k_1 - m\lambda)(k_2 - m\lambda) - k_3^2 = 0 \quad (16)$$

and

$$\begin{aligned} \lambda_3 &= \frac{k_1 + k_2 - \sqrt{(k_1 - k_2)^2 + 4k_3^2}}{2m}, \\ \lambda_4 &= \frac{k_1 + k_2 + \sqrt{(k_1 - k_2)^2 + 4k_3^2}}{2m}. \end{aligned} \quad (17)$$

We also obtain:

$$\begin{aligned} \zeta_3 &= 1 - \frac{3}{2} \cos^2 \gamma, \\ \zeta_4 &= 1 - \frac{3}{2} \sin^2 \gamma, \end{aligned} \quad (18)$$

hence,

$$\zeta_3 + \zeta_4 = \frac{1}{2}. \quad (19)$$

For XY_4 molecules [25, 29], we have:

$$\begin{aligned} \cos \gamma &= \frac{1}{\sqrt{2}} \left[1 + \frac{k_2 - k_1}{\sqrt{(k_2 - k_1)^2 + 4k_3^2}} \right]^{1/2}, \\ \sin \gamma &= \frac{1}{\sqrt{2}} \left[1 - \frac{k_2 - k_1}{\sqrt{(k_2 - k_1)^2 + 4k_3^2}} \right]^{1/2}, \end{aligned} \quad (20)$$

noting that for the XY_6 molecules, Moret Bailly [29] switched $\cos \gamma$ and $\sin \gamma$.

Some additional relations are given in Appendix 2.

We can also deduce from formulas (17)–(20):

$$\begin{aligned}\lambda_3 + \lambda_4 &= \frac{k_1 + k_2}{m}, \\ \lambda_3 \zeta_3 + \lambda_4 \zeta_4 &= \frac{k_1}{m} - \frac{k_2}{2m}, \\ \lambda_3 \lambda_4 &= \frac{1}{m^2} (k_1 k_2 - k_3^2).\end{aligned}\tag{21}$$

The system of equations (6), (8) and (11) becomes:

$$\begin{aligned}G_{33}F_{33} + G_{44}F_{44} + 2G_{34}F_{34} &= \frac{k_1 + k_2}{m}, \\ C_{33}F_{33} + C_{44}F_{44} + 2C_{34}F_{34} &= \frac{k_1}{m} - \frac{k_2}{2m}, \\ F_{33} - 2F_{44} + F_{34} &= \frac{3}{2} \sqrt{\frac{2\mu}{m}} \epsilon |k_3|.\end{aligned}\tag{22}$$

By solving the system, we obtain:

$$\begin{aligned}F_{33} &= \alpha k_1 + \frac{2}{3} k_2 + \frac{2}{3} \beta \epsilon |k_3|, \\ F_{44} &= \alpha k_1 + \frac{1}{6} k_2 - \frac{1}{3} \beta \epsilon |k_3|, \\ F_{34} &= \alpha k_1 - \frac{1}{3} k_2 + \frac{1}{6} \beta \epsilon |k_3|,\end{aligned}\tag{23}$$

75 with

$$\alpha = \frac{\mu}{3m}, \quad \beta = \sqrt{\frac{2\mu}{m}}.\tag{24}$$

4. Isotopic relations in Cartesian coordinates

As for the force constants F_{ij} , the k_2 constant is invariant relative to isotopic substitutions as far as ${}^cS_{4\alpha}$ coordinates do not depend of masses.

Therefore, we can write:

$$\begin{aligned}\alpha k_1 + \frac{2}{3} \beta \epsilon |k_3| &= \alpha' k'_1 + \frac{2}{3} \beta' \epsilon' |k'_3|, \\ \alpha k_1 - \frac{1}{3} \beta \epsilon |k_3| &= \alpha' k'_1 - \frac{1}{3} \beta' \epsilon' |k'_3|\end{aligned}\tag{25}$$

and so:

$$\beta \epsilon |k_3| = \beta' \epsilon' |k'_3|.\tag{26}$$

80 However, in the relations from (17) to (20), allowing to calculate frequencies and Coriolis constants, only the parameter k_3^2 is needed. Consequently,

$$\beta^2 \epsilon^2 |k_3|^2 = \beta'^2 \epsilon'^2 |k'_3|^2\tag{27}$$

and thus,

$$\beta^2 k_3^2 = \beta'^2 k_3'^2, \quad (28)$$

Then $k_3'^2$ can be expressed as

$$k_3'^2 = \frac{\mu}{\mu'} \frac{m'}{m} k_3^2. \quad (29)$$

Also, from equation (25) we show that:

$$k_1' = \frac{\mu}{\mu'} \frac{m'}{m} k_1, \quad (30)$$

85 and

$$k_2' = k_2. \quad (31)$$

From formula (32) below, deduced from relations (21), we can calculate k_1 , k_2 and k_3^2 constants for one isotopologue that we know λ_3 and λ_4 frequencies and ζ_3 or ζ_4 Coriolis constants, and apply isotopic relations (29) to (31) to compute frequencies and Coriolis parameters of other isotopologues using formula (17) to (20):

$$\begin{aligned} \frac{3}{2} \frac{k_1}{m} &= \lambda_3 \left(\zeta_3 + \frac{1}{2} \right) + \lambda_4 \left(\zeta_4 + \frac{1}{2} \right), \\ \frac{k_2}{m} &= \lambda_3 + \lambda_4 - \frac{k_1}{m}, \\ k_3^2 &= k_1 k_2 - m^2 \lambda_3 \lambda_4. \end{aligned} \quad (32)$$

90 Moreover, we have shown that isotopic relations (29) to (31) are independant of ϵ . Then, using *GF* method, both set of parameters F_{ij} (for $\epsilon = \pm 1$) obtained by (12) lead to the same frequency values and Coriolis constants (λ_s and ζ_s) for one isotopologue.

5. Application to XY_4 molecules

95 We present here applications of the previous formulas to three tetrahedral spherical-top molecules: methane (CH_4), germane (GeH_4) and ruthenium tetroxide (RuO_4).

Table 1: Band center and Coriolis ζ constant for the ν_3 and ν_4 fundamental bands of different tetrahedral methane isotopologues. We use experimental values for $^{12}\text{CH}_4$ from Ref. [32] as the strating point to calculate values for the other isotopologues and compare with literature values. Two calculations are made in each case: one using experimentally fitted band centers (ν) and ζ constants and one using calculated harmonic frequencies (ω , estimated by authors from the experimental values of ν and of the anharmonic constants X) and ζ constants. For these two calculations, the ζ constants are denoted ζ^{ν} and ζ^{ω} , respectively.

Isotopologue	ν_3/cm^{-1}		ω_3/cm^{-1}		ζ_3^{ν}		ζ_3^{ω}		ν_4/cm^{-1}		$\zeta_4^{\nu\dagger}$		ζ_4^{ω}	
	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc
$^{12}\text{CH}_4$ [32]	3019.2	3019.20	3156.8	3156.80	0.054	0.056	0.046	0.046	1310.8	1310.80	1367.4	1367.40	0.446	0.454
$(\zeta_3^{\nu} + \zeta_4^{\nu})_{\text{exp}} = 0.508$														
$^{13}\text{CH}_4$ [32–34]	3009.5	3008.45	3146.6	3145.76	0.045	0.046	0.036	0.036	1302.8	1302.77	1358.9	1358.94	0.455	0.464
$(\zeta_3^{\nu} + \zeta_4^{\nu})_{\text{exp}} = 0.509$														
$^{12}\text{CD}_4$ [32]	2260.1	2234.47	2336.2	2334.86	0.163	0.173	0.165	0.165	997.8	990.10	1034.1	1033.49	0.337	0.335
$(\zeta_3^{\nu} + \zeta_4^{\nu})_{\text{exp}} = 0.500$														
$^{12}\text{CT}_4$ [35]	1937.0	1906.52	1993.9	1991.10	0.252	0.275	0.266	0.266	858.0	847.45	880.1	885.07	0.248	0.234
$(\zeta_3^{\nu} + \zeta_4^{\nu})_{\text{exp}} = 0.500$														

\dagger We take here $\zeta_4^{\nu} = 1/2 - \zeta_3^{\nu}$ as the “experimental” value; the “true” experimental ζ sum is given at the beginning of the line.

Methane is of course a very important hydrocarbon molecule for many applications in atmospheric and astrophysical sciences, whose spectroscopy is extensively studied (see [5, 36] and references therein). There already exist many studies concerning its different isotopologues. We use it here as a simple illustration example. Recent studies [5, 36] use sophisticated effective
100 Hamiltonians that take into account the complex polyad structure of this molecule, with many intra-polyad interactions (Fermi resonances, Coriolis interactions between different bands, *etc.*). Their parameters are not easily usable for the present simple application since one would need to extract decorrelated band centers and Coriolis constants. We rather use here simpler old studies that considered fits of the ν_3 and ν_4 bands as isolated. If the accuracy is not as high as what
105 can be done nowadays, this is largely sufficient for simple low order calculations like the present ones. We thus start from $^{12}\text{CH}_4$ values taken from Ref. [32] and then deduce, using the method explained in Sections 3 and 4, the corresponding constants for $^{13}\text{CH}_4$, $^{12}\text{CD}_4$ and $^{12}\text{CT}_4$. The results are compared to the literature [32–35]. This is presented in Table 1.

Some important points should be noticed:

- 110 • The method described in Section 2 using internal coordinates gives exactly the same results, within numerical rounding errors. The two choices for ϵ (± 1) give different force constants F , but the same band center and Coriolis constant values. The cartesian coordinate method (Section 4), as it does not depend on ϵ , does not have this drawback.
- 115 • In principle, calculations should use the harmonic wavenumbers ω . As an approximation, we can also use the band center ν , knowing that the fitted effective hamiltonian parameter ν corresponds to the true band center ($J = 0$ level) only when bands are studied as isolated. As we can see in Table 1, both calculations work well, the one using harmonic wavenumbers ω being significantly better, considering the relative isotopic shift error. For instance, the error on the $^{12}\text{CH}_4 \rightarrow ^{12}\text{CD}_4$ shift is 3.3 % for ν_3 and better for ω_3 , as expected for our
120 simple model. The result is similar for ν_4 .
- For high-resolution, more elaborated but heavier models should be used, like for instance that of Rey *et al.* [37]. We can notice, however, from Table 9 of this reference, that we get very similar $^{12}\text{CH}_4 \rightarrow ^{12}\text{CD}_4$ isotopic shifts for ν_3 and ν_4 band centers, taking into account the expected accuracy of our simple model.
- 125 • According to the correspondance between the Dijon tensorial formalism [2–4] (used for the fits) and “classical” notations, [2, 38] we have

$$t_{\{i\}\{i\}}^{1(1,0F_1)} = 3\sqrt{2}(B\zeta)_i, \quad (33)$$

(with $i = 3$ or 4) for the tensorial Coriolis parameter. We use this relation to estimate the ζ value, with the approximation

$$(B\zeta)_i \simeq B_0\zeta_i, \quad (34)$$

B_0 being the ground state rotational constant.

- 130 • The Coriolis constants ζ should follow the sum rule (19). However, when using such constants resulting from independent fits of ν_3 and ν_4 spectroscopic data, this sum rule is generally only approximately respected (within a few %). The present calculations proved to give better results if we make the following choice: (i) we take the experimental ζ_3 value obtained through (33) and (34) and (ii) we use

$$\zeta_4 = \frac{1}{2} - \zeta_3. \quad (35)$$

135 This only slightly differ from the experimental ζ_4 value and is more consistent with the
 present method that is based on the sum rule.

Our second exemple is GeH_4 . The fundamental bands of this molecule, which is of importance in planetology (see [9] and references therein) have been recently studied in our group [9, 10]. In this case, we do not have anharmonic constants and thus ω values cannot be obtained. But band centers are well determined and ν are convenient. Moreover, for this molecule, 140 no strong Fermi resonance is observed between bending and stretching modes. The ν_3 and ν_4 constants are obtained through fits of two dyads, ν_2/ν_4 [10] and ν_1/ν_3 [9], which only present limited rovibrational interactions of Coriolis type. Thus, the fitted values of ν_3 and ν_4 are almost identical to band centers as it can be verified by calculating the $J = 0$ levels.

145 Germanium in natural abundance presents 5 isotopes. We can thus calculate germane force constants using experimental ν_3 , ν_4 , ζ_3 and ζ_4 values (with the same remarks as for methane above) for $^{70}\text{GeH}_4$ and then deduce these constants for $^{72}\text{GeH}_4$, $^{73}\text{GeH}_4$, $^{74}\text{GeH}_4$ and $^{76}\text{GeH}_4$ and compare them to the experiment. The results are presented on Figure 2. Taking into account the many approximations made, the results are very satisfying. The relative error on isotopic shifts is small. We also notice on the lower right panel the limited error on the ζ sum rule. The experimental ζ_4 value is shifted from the $1/2 - \zeta_3$ value, but follows the same tendency.

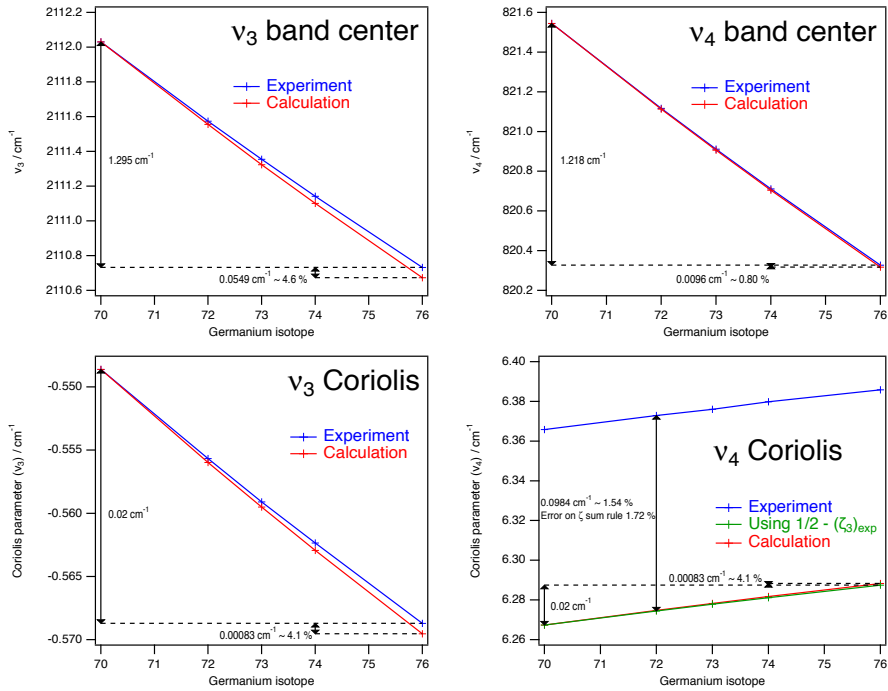


Figure 2: The band center and Coriolis constant ($3\sqrt{2}B\zeta_i$, see text) as a function of the germanium isotope for the GeH_4 molecule. Blue curves show the values fitted on experimental spectra; the red curves show the calculated values determined from the $^{70}\text{GeH}_4$ experimental value. In the case of ζ_4 , we used the $1/2 - \zeta_3$ value (green curve), the experimental value being farther away from this sum rule. We also indicate the resulting relative error for the $^{76}\text{GeH}_4$ isotopologue.

The third example that we show here is ruthenium tetroxide. This molecule is of importance for nuclear power plant security and other industrial applications (see [13, 23, 39] and references therein). In natural abundance, it possesses 5 isotopologues, due to the different ruthenium isotope (we do not consider here oxygen isotopes): $^{99}\text{RuO}_4$, $^{100}\text{RuO}_4$, $^{101}\text{RuO}_4$, $^{102}\text{RuO}_4$ (the main one) and $^{104}\text{RuO}_4$. There are also two isotopologues with very low abundance, namely $^{97}\text{RuO}_4$ and $^{98}\text{RuO}_4$ and two radioactive, short-lived, isotopologues, $^{103}\text{RuO}_4$ and $^{106}\text{RuO}_4$.

In Ref. [13], we analyzed in detail the ν_3 band for all observable isotopologues and extrapolated the band center and Coriolis parameter for the others. In Ref. [23], we analyzed the ν_2/ν_4 bending dyad for $^{102}\text{RuO}_4$ only. We can thus apply the same method by starting with $^{102}\text{RuO}_4$ values. As for germane, we use band centers, the ω values being unknown and we also consider ζ_4 as $1/2 - \zeta_3$ (the ζ sum with the experimental ζ_4 value [23] being 0.484). The calculated results are compared with experimental and extrapolated values from Ref. [13] on Figure 3. Again, the results are very satisfying, with small errors on isotopic shifts; values are very close to those of Ref. [13]. It is then possible to deduce values for the ν_4 band for the different isotopologues that, apart from $^{102}\text{RuO}_4$, have not yet been analyzed up to now. As an illustration, Table 2 gives the ν_4 predicted band centers and Coriolis constants. For these ones, we can calculate the difference between the experimental parameter for $^{102}\text{RuO}_4$ [23] and the $1/2 - \zeta_3$ value used in the present calculation; then we predict ζ_4 value, say ζ_4^p thanks to the calculated value ζ_4^c obtained in the present paper through:

$$\zeta_4^p = \zeta_4^c + \Delta\zeta_4. \quad (36)$$

As we saw for GeH_4 (lower right panel of Figure 2), the variation of the experimental and calculated (starting from $1/2 - \zeta_3$ for the reference isotopologue) value of ζ_4 are parallel; it is thus justified to apply the same correction $\Delta\zeta_4$ to all isotopologues. The tensorial constant is also evaluated by multiplying ζ_4^p by $3\sqrt{2}B_0$.

Isotopologue	ν_4 / cm^{-1}	ζ_4^p	$t_{\{4\}\{4\}}^{1(1,0F_1)} / \text{cm}^{-1}$
$^{97}\text{RuO}_4$	337.047	0.2808	0.1618
$^{98}\text{RuO}_4$	336.683	0.2828	0.1629
$^{99}\text{RuO}_4$	336.325	0.2848	0.1641
$^{100}\text{RuO}_4$	335.972	0.2867	0.1652
$^{101}\text{RuO}_4$	335.623	0.2886	0.1663
$^{102}\text{RuO}_4$	335.281	0.2904	0.1673
$^{103}\text{RuO}_4$	334.942	0.2922	0.1684
$^{104}\text{RuO}_4$	334.609	0.2940	0.1694
$^{106}\text{RuO}_4$	333.957	0.2976	0.1714

Table 2: Predicted ν_4 band centers and Coriolis constants (see text for notations) for the different isotopologues of RuO_4 . The reference isotopologue is $^{102}\text{RuO}_4$, so the values given here for this one are identical to the experimental ones [13].

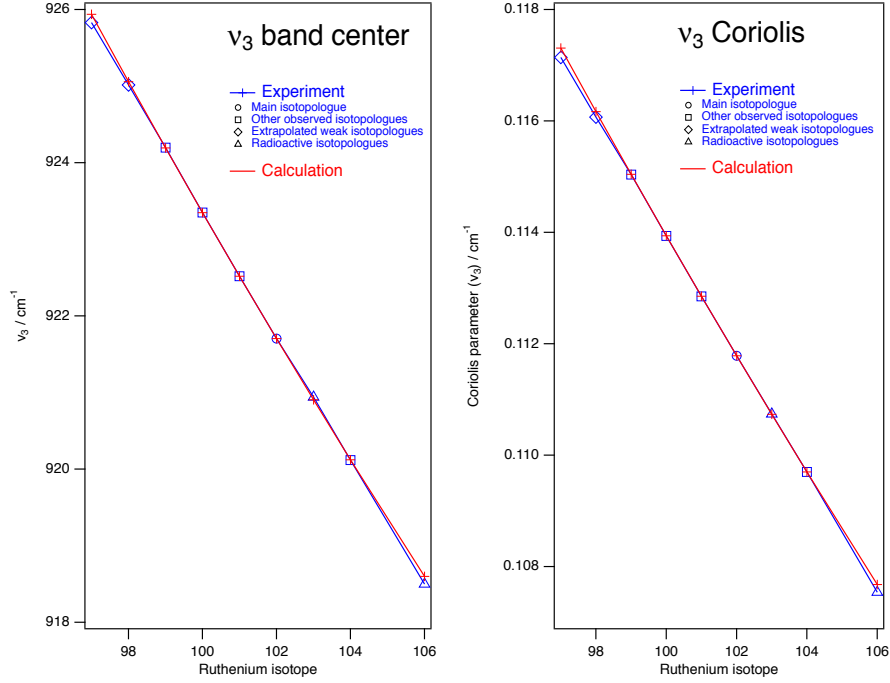


Figure 3: The band center and Coriolis constant ($3\sqrt{2}B\zeta_3$, see text) as a function of the ruthenium isotope for the ν_3 band of the RuO_4 molecule. We use symbols to distinguish between observed and extrapolated data for the different isotopologues.

175 6. Application to XY_6 molecules

Formula established for XY_4 molecules can be applied to XY_6 molecules by simply replacing G , C and μ by [26, 40–42]:

$$G = \begin{pmatrix} \frac{2}{M} + \frac{1}{m} & \frac{4}{M} \\ \frac{4}{M} & \frac{8}{M} + \frac{2}{m} \end{pmatrix}, C = \begin{pmatrix} \frac{2}{M} & -\frac{1}{m} - \frac{4}{M} \\ -\frac{1}{m} - \frac{4}{M} & \frac{1}{m} + \frac{8}{M} \end{pmatrix} \quad (37)$$

and

$$\mu = \frac{mM}{M + 6m}. \quad (38)$$

In this case, the ν_3 and ν_4 normal mode coordinates possess the F_{1u} symmetry in the O_h point group.

We can thus apply the present theory to the SF_6 molecule. This one is a very strong greenhouse gas, see [17] and references therein. It possesses four isotopologues in natural abundance, namely $^{32}\text{SF}_6$, $^{33}\text{SF}_6$, $^{34}\text{SF}_6$ and $^{36}\text{SF}_6$, the latter one having a very small abundance of only 0.02 % [22]. We can thus use the very accurate values for $^{32}\text{SF}_6$ (using band centers as for germane above) to deduce the constants for the other isotopologues and compare them to experimental values, when available. The results are presented on Figure 4 and, again, are very

satisfying. We see here that this method allows to estimate constants that are not known for some minor isotopologues and serve as a starting point for their future analysis.

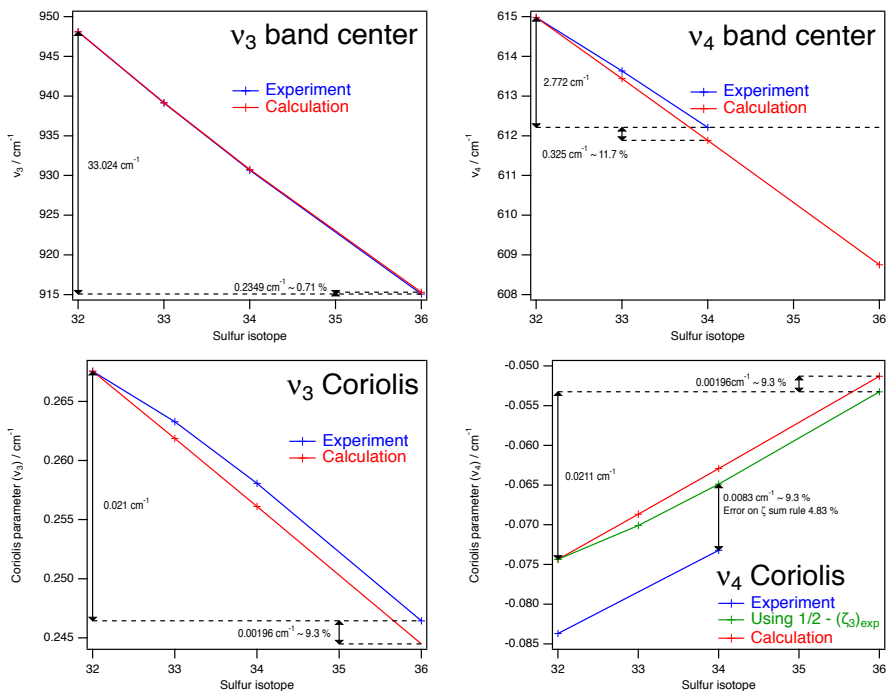


Figure 4: The band center and Coriolis constant ($3\sqrt{2}(B\zeta)$, see text) as a function of the sulfur isotope for the SF₆ molecule. The legend is the same as for Figure 2. In this case, no data exist for the ν_4 band of $^{36}\text{SF}_6$. As for $^{33}\text{SF}_6$ the ν_4 band center is an extrapolated value from Ref. [43], while the Coriolis constant is no known.

7. Conclusion

190 We have shown that isotopic relations, when established in the Cartesian coordinate system for tetrahedral and octahedral molecules, lead to simple calculations for harmonic and Coriolis constants. As a matter of fact, these calculations depend only on masses (μ and m) and not on the whole G and C matrices as when using the internal coordinate system.

195 We have also shown that the ambiguity on the determination of force constants is not involved in these isotopic relations. Moreover, it should be noticed that the ambiguity in Cartesian coordinates only resides in the sign of the interaction parameter $k_{34} = k_3$, while for internal coordinates, the three force constants lead to three different values when changing the sign of ϵ .

200 Finally, we have illustrated the use of the simple isotopic relations developed here for a few tetrahedral molecules and for octahedral SF₆. Such relations can be of help to make initial predictions for various rare isotopologues of spherical top molecules, provided that one main isotopologue is well known.

Appendix 1: Formulas for the *GF* method

Following the *G* and *C* matrix definition from Equation (10), Equation (9) becomes

$$F_{33} - 2F_{44} + F_{34} = \mu m D, \quad (39)$$

with

$$\mu = \frac{mM}{M + 4m}, \quad (40)$$

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$$D = \epsilon(\lambda_3 - \lambda_4) \sqrt{\zeta_3 \zeta_4 |G| - |C|}, \quad (41)$$

$$|G| = -2|C| = \frac{2}{\mu m}, \quad (42)$$

whence

$$D = \epsilon(\lambda_3 - \lambda_4) |G|^{1/2} \sqrt{\zeta_3 \zeta_4 + \frac{1}{2}}. \quad (43)$$

According the sum rules for spherical tops [28, 40, 44, 45]

$$\zeta_3 + \zeta_4 = \frac{1}{2} \quad (44)$$

and

$$\zeta_3 \zeta_4 + 1 = (1 - \zeta_4) \left(\frac{1}{2} + \zeta_4 \right). \quad (45)$$

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In addition, we have:

$$\lambda_3 \zeta_3 + \lambda_4 \zeta_4 = \frac{1}{4} (\lambda_3 + \lambda_4) - \frac{1}{4} (4\zeta_4 - 1) (\lambda_3 - \lambda_4). \quad (46)$$

Appendix 2: Relations in terms of Cartesian force constants

From ζ_3 and ζ_4 (cf. Eq. (18)) and noticing that $\sin 2\gamma$ is positive by definition, we deduce:

$$\begin{aligned} \cos 2\gamma &= \frac{1}{3} (4\zeta_4 - 1), \\ \sin 2\gamma &= \frac{4}{3} \sqrt{(1 - \zeta_4) \left(\frac{1}{2} + \zeta_4 \right)}. \end{aligned} \quad (47)$$

Then, from $\cos \gamma$ and $\sin \gamma$ from Eq. (20) we obtain the following relations:

$$\begin{aligned} \cos 2\gamma &= \frac{k_2 - k_1}{k}, \\ \sin 2\gamma &= \frac{2|k_3|}{k}, \end{aligned} \quad (48)$$

with

$$k = \sqrt{(k_2 - k_1)^2 + 4k_3^2}. \quad (49)$$

In addition,

$$m(\lambda_3 - \lambda_4) = k. \quad (50)$$

So,

$$\begin{aligned} \mu m D &= \epsilon(\lambda_3 - \lambda_4) \sqrt{2\mu m (1 - \zeta_4) \left(\frac{1}{2} + \zeta_4\right)} \\ &= \frac{3}{2} \sqrt{\frac{2\mu}{m}} \epsilon |k_3|. \end{aligned} \quad (51)$$

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