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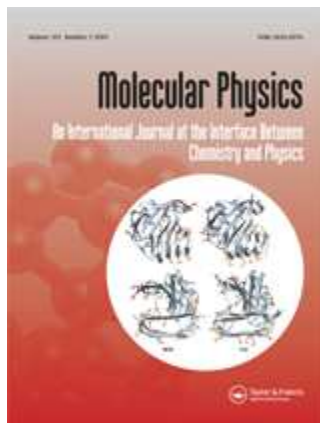
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Spin-rotation and nuclear shielding constants of sulfur hexafluoride

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Abstract

We present a first theoretical determination of the hyperfine coupling constants of a spherical top molecule, using *ab initio* methods. The scalar and the tensorial contributions to the spin-rotation constants and the diamagnetic and paramagnetic contributions to the nuclear shielding constant are calculated for the $^{32}\text{SF}_6$ molecule. The corrections to the spin-rotation constants due to the nuclear Thomas precession are evaluated and discussed. Our results are compared with previously reported experimental values.

Key words: Ab initio calculations, spin-rotation constants, hexafluoride

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1 Introduction

Studies concerning the molecule SF_6 are of considerable interest from several points of view. For example, control of SF_6 in the atmosphere is fundamental for environmental security in such way, that the Kyoto protocol regulates the allowable values. Effectively, in spite of being non-toxic, non-corrosive, and a chemical gas that does not destroy the ozone layer, it has a powerful greenhouse effect and a global warming power, much larger than CO_2 over a longtime horizon.

The S^{19}F_6 molecule is an octahedral type molecule with a central spinless S atom and outside 1/2 spin F nuclei. The study of magnetic hyperfine structures

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1 detected in highly symmetric molecules like this has progressed enormously
2 in the seventh and eighth decades of last century. Some of the fundamental
3 tools for that progress were the ultra-high resolution infrared spectroscopy
4 [1–3] and the development of a tensorial formalism suitable for the interpre-
5 tation of the measured spectra [4–8]. However, the theoretical determination
6 of the electronic contribution to the nuclear hyperfine constants included in
7 the hamiltonian that describes the magnetic hyperfine structures, could not
8 be achieved in those days due to the impossibility of achieving sufficiently
9 accurate calculations. Therefore, comparison with experimental results could
10 not be completely done.

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12 Recent progress on derivative techniques together with *ab initio* methods have
13 enhanced the possibility of performing those kind of calculations. Particularly,
14 for the spin-rotation constants, it has been shown by Gauss, Ruud and Hel-
15 gaker [9] that the combination of derivative techniques with rotational London
16 orbitals gives a suitable method of calculation.

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19 In the present work we have used derivative techniques and *ab initio* methods
20 to calculate the spin-rotation constants of the SF₆ molecule. We have cal-
21 culated separately the nuclear and electronic contribution to these constants
22 and discussed the influence of the Thomas precession factor as well [10]. In
23 addition, we have calculated the shielding tensor, and discussed its relation-
24 ship with the spin-rotation tensor, as firstly established by Ramsey [11] for
25 diatomic molecules and generalized by Flygare for polyatomic molecules [12].
26 We have also discusses the basis sets more suitable for the study of the SF₆
27 molecule. The utilization of rotational London orbitals has been proven to be
28 essential to get significative results. A comparison with the available experi-
29 mental results is presented here. Effects due to the molecule vibration will not
30 be considered in this work.

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33 This work represents the first step on the calculation of spin-rotation and
34 shielding constants of spherical top molecules using *ab initio* methods and
35 derivative techniques.

36 37 38 39 40 41 42 43 **2 Formalism and conventions**

44 45 46 *2.1 The spin-rotation hamiltonian*

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49 The study of magnetic interactions in molecules in their ground electronic
50 state, and particularly of the spin-rotation interaction and its relationship
51 with paramagnetic shielding, has been extensively developed in early works
52 where a fundamental physical description of these interactions has been es-
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published [12]. A general study of nuclear hyperfine interactions in molecules, including effects due to the molecular vibration and centrifugal distortion has been reported by Michelot [13,14]. Although in this study we will not take into account molecular vibration, we will adopt some of the very general formulae of this author, which facilitates the discussion of the relationship between the paramagnetic parts of the spin-rotation and the shielding tensor.

The spin-rotation hamiltonian, \mathbf{H}_{SR} , describes the interactions between the magnetic momentum of each nucleus N and the magnetic field created at that nucleus by the relative motion of the electrons and the other nuclei in the molecule. On the other hand, this magnetic field at nucleus N is related to the total rotational angular momentum \mathbf{J} through the spin-rotation tensor ${}^N\mathbf{C}$. Therefore, we can write (the International System of Units, SI, is adopted hereafter)

$$\mathbf{H}_{\text{SR}} = - \sum_N \mathbf{I}_N \cdot {}^N\mathbf{C} \cdot \mathbf{J}, \quad (1)$$

where \mathbf{I}_N is the nuclear spin angular momentum of nucleus N .

The tensor ${}^N\mathbf{C}$ may be represented by the sum of a purely nuclear contribution, ${}^N\mathbf{C}^n$, and an electronic contribution, ${}^N\mathbf{C}^e$, depending upon the electronic variables,

$${}^N\mathbf{C} = {}^N\mathbf{C}^n + {}^N\mathbf{C}^e, \quad (2)$$

where, the nuclear contribution is given by

$${}^N\mathbf{C}^n = \sum_{K \neq N} \frac{\hbar g_N Z_K \mu_n e}{4\pi \epsilon_0 c^2} \left\{ \left(\frac{\mathbf{r}_{NK}}{r_{NK}^3} \cdot [\gamma_N^T \mathbf{r}_N - \mathbf{r}_K] \right) \mathbf{I}^{-1} - [\gamma_N^T \mathbf{r}_N - \mathbf{r}_K] \frac{\mathbf{r}_{NK}}{r_{NK}^3} \cdot \mathbf{I}^{-1} \right\}. \quad (3)$$

Here, Z_N , r_N , m_N and g_N are, respectively, the atomic number, position, mass and the nuclear g factor of the N nucleus. e , μ_n and c are the electronic charge, nuclear magneton $\mu_n = \frac{e\hbar}{2m_p}$ and velocity of light, respectively. m_p is the mass of the proton, and \mathbf{I} is the inertia tensor.

The electronic contribution is equal to the sum of a diamagnetic term, ${}^N\mathbf{C}^{\text{ed}}$, involving only the electronic functions of the fundamental electronic state, and a paramagnetic term, ${}^N\mathbf{C}^{\text{ep}}$, involving those of the other electronic states,

$${}^N\mathbf{C}^e = {}^N\mathbf{C}^{\text{ed}} + {}^N\mathbf{C}^{\text{ep}}, \quad (4)$$

where

$${}^N\mathbf{C}^{\text{ed}} = \sum_i \frac{\hbar e g_N \mu_n}{4\pi\epsilon_0 c^2} \gamma_N^T \left\langle 0 \left| \left(\frac{\mathbf{r}_{iN}}{r_{iN}^3} \cdot \mathbf{r}_N \right) \mathbf{I}^{-1} - \mathbf{r}_N \left(\frac{\mathbf{r}_{iN}}{r_{iN}^3} \cdot \mathbf{I}^{-1} \right) \right| 0 \right\rangle. \quad (5)$$

and

$${}^N\mathbf{C}^{\text{ep}} = \sum_{p \neq 0} \frac{\hbar e g_N \mu_n}{4\pi\epsilon_0 m c^2} (V_0 - V_p)^{-1} \left[\langle 0 | \mathbf{L}' | p \rangle \langle p | \mathbf{L} \cdot \mathbf{I}^{-1} | 0 \rangle + \langle 0 | \mathbf{L} \cdot \mathbf{I}^{-1} | p \rangle \langle p | \mathbf{L}' | 0 \rangle \right]. \quad (6)$$

The index i stands for an electron, m for its mass, $|0\rangle$ and $|p\rangle$ represents the fundamental electronic state and an arbitrary electronic p state, respectively.

The electronic angular momentum, \mathbf{L} , and the closely related operator \mathbf{L}' , are given, respectively, by

$$\mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i \quad (7)$$

and

$$\mathbf{L}' = \sum_i \frac{\mathbf{r}_{iN}}{r_{iN}^3} \times \mathbf{p}_i. \quad (8)$$

The correction due to Thomas precession [10] corresponds to the introduction of the following corrective factor in the diamagnetic contribution to the spin-rotation tensor

$$\gamma_N^T = \left(1 - \frac{Z_N m_p}{g_N m_N} \right). \quad (9)$$

In the above expressions for the coefficients of the spin-rotation tensor all vector quantities are relative to the molecular center of mass.

It has been shown by Flygare [12] that it is possible to eliminate the term given by Equation (5) by referring the operators defined by Equations (7) and (8) to the N nucleus. The aim of such transformation, which has been extensively used in later works, is to obtain a more easily calculable relation between the spin-rotation and the shielding tensors. However, this transformation was not used in this work since the paramagnetic terms are evaluated around the center of mass.

It should be mentioned that the evaluation of expressions like Equation (6) corresponding to second-order corrections to the electronic hamiltonian operator, usually called second-order properties, is very inefficient in *ab initio* methods; these second-order properties are usually calculated by derivative methods based on the Hellman-Feynman theorem.

Specifically, the calculation of the second derivatives of the electronic energy

E^{et} with respect to I and J gives a suitable method to obtain this contribution [9],

$${}^N\mathbf{C}^e = - \left(\frac{\partial^2 E^{\text{et}}}{\partial I_N \partial J} \right)_{I_N J=0}. \quad (10)$$

2.2 Symmetry considerations

The non-vanishing elements of the tensor ${}^N\mathbf{C}$ (and obviously of each of the tensors ${}^N\mathbf{C}^n$ and ${}^N\mathbf{C}^e$) are determined by symmetry considerations of the magnetic field detected at each nuclear site. In the case of an octahedral-type molecule like the SF_6 , we can follow the discussion given in reference [5].

Let us consider a molecule fixed frame, $Oxyz$, with two F nuclei symmetrically located on each axis (two fluor nucleus, F_1 and F_2 , at positions $+a, -a$ on the x axis, two fluor nucleus, F_3 and F_4 , at positions $+a, -a$ on the y axis and two fluor nucleus, F_5 and F_6 , at positions $+a, -a$ on the z axis), and the S nucleus at the origin.

The J_α ($\alpha = x, y$ or z) angular momentum component will generate a magnetic field directed along the α axis. Moreover, for a nucleus on the γ axis (with $\gamma \neq \alpha, \beta$), the J_α and J_β components will create identical effects; $(\alpha, \beta, \gamma) \equiv (x, y, z)$. It is then easily shown that the ${}^N\mathbf{C}$ tensor may be written as a sum of a scalar and a tensorial contribution,

$${}^N\mathbf{C} = c_a \mathbf{1} + \frac{1}{3} c_d {}^N\boldsymbol{\varepsilon}, \quad (11)$$

where c_a and c_d are, respectively, the scalar, or average spin-rotation constant, and the tensor spin-rotation constant, or anisotropy in the spin-rotation tensor. $\mathbf{1}$ is the identity tensor and ${}^N\boldsymbol{\varepsilon}$ are second-rank diagonal traceless tensors with elements ${}^N\varepsilon_{\alpha\alpha} = -2$, if the nucleus N is on axis α , and ${}^N\varepsilon_{\alpha\alpha} = 1$, if the nucleus N is on axis β or γ ($\beta, \gamma \neq \alpha$). More specifically, in the case of the adopted $Oxyz$ frame,

$${}^1\varepsilon = {}^2\varepsilon = \begin{pmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad {}^3\varepsilon = {}^4\varepsilon = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad {}^5\varepsilon = {}^6\varepsilon = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \quad (12)$$

and the c_a can be obtained from the ${}^N\mathbf{C}$ tensor of any nuclei N ,

$$c_a = \frac{1}{3} \text{Tr } {}^N\mathbf{C}. \quad (13)$$

For either of the two nuclei N on the axis α with $\beta \neq \alpha$, we have

$$c_d = {}^N C^{\beta\beta} - {}^N C^{\alpha\alpha}. \quad (14)$$

According to Equation (2), we have

$$c_a = c_a^n + c_a^e \quad (15)$$

and

$$c_d = c_d^n + c_d^e, \quad (16)$$

where c_a^n (c_a^e) and c_d^n (c_d^e) are the scalar and the tensorial contribution to the nuclear (electronic) spin-rotation constants, respectively. For c_a^e and c_d^e , we have also the corresponding decomposition in diamagnetic and paramagnetic parts, i.e.,

$$c_a^e = c_a^{ed} + c_a^{ep} \quad (17)$$

and

$$c_d^e = c_d^{ed} + c_d^{ep}. \quad (18)$$

2.3 The shielding hamiltonian

Ramsey in his seminal paper entitled "Magnetic shielding of nuclei in molecules" [11] has shown that the effect of shielding can be expressed as a sum of a diamagnetic term, similar to the Lamb expression for atoms, and a second order paramagnetic term. The evaluation of this paramagnetic term has motivated several works, many of them taking advantage of its relationship with the spin-rotation interaction measurement results.

The shielding hamiltonian may be represented by

$$\mathbf{H}_{SH} = \mu_n \sum_N g_N \mathbf{I}_N \cdot {}^N \sigma \cdot \mathbf{B}, \quad (19)$$

where \mathbf{B} is the external applied magnetic field. There is a diamagnetic, ${}^N \sigma^d$, and a paramagnetic contribution, ${}^N \sigma^p$, to the shielding tensor ${}^N \sigma$,

$${}^N \sigma = {}^N \sigma^d + {}^N \sigma^p, \quad (20)$$

where

$${}^N \sigma^d = \sum_i \frac{e^2}{8\pi\epsilon_0 m c^2} \left\langle 0 \left| \frac{\mathbf{r}_{iN} \cdot \mathbf{r}_i}{r_{iN}^3} \mathbf{1} - \frac{\mathbf{r}_{iN}}{r_{iN}^3} \mathbf{r}_i \right| 0 \right\rangle \quad (21)$$

and

$${}^N \sigma^p = -\frac{e^2}{8\pi\epsilon_0 m^2 c^2} \sum_{p \neq 0} (V_p - V_0)^{-1} \left\{ \langle 0 | \mathbf{L}' | p \rangle \langle p | \mathbf{L} | 0 \rangle + [\langle 0 | \mathbf{L}' | p \rangle \langle p | \mathbf{L} | 0 \rangle]^* \right\}. \quad (22)$$

The relationship between the paramagnetic component of the shielding and the spin-rotation tensors for this kind of molecule is directly obtained by comparing Equation (6) and Equation (22),

$${}^N\sigma^p = \frac{1}{2\gamma_N} {}^N\mathbf{C}^{ep} \cdot \mathbf{I}, \quad (23)$$

where γ_N is given by (in S.I.) $\gamma_N = \frac{m}{e} \hbar \mu_n g_N$.

Therefore, we may write the following simple relationship between the spin-rotation and the shielding tensors:

$${}^N\mathbf{C} - {}^N\mathbf{C}^n = {}^N\mathbf{C}^{ed} + 2\gamma_N ({}^N\sigma - {}^N\sigma^d) \cdot \mathbf{I}^{-1}. \quad (24)$$

We note that for spherical tops the inertia tensor is proportional to the identity matrix, i.e., $\mathbf{I} = I\mathbf{1}$. From symmetry considerations, the shielding tensor ${}^N\sigma$ can also be written as a sum of a scalar and a tensorial part, like Equation (11). However, for performing a comparison with previous works on chemical shifts or nuclear magnetic resonance, we only present the results concerning the average diamagnetic and paramagnetic shieldings for the nucleus N, namely

$${}^N\sigma_a^d = \frac{1}{3} \text{Tr} ({}^N\sigma^d) \quad (25)$$

and

$${}^N\sigma_a^p = \frac{1}{3} \text{Tr} ({}^N\sigma^p). \quad (26)$$

3 Computational details

All calculations were performed at the Hartree-Fock (HF) level on a IBM RISC/6000 workstation using the Dalton program package (Release 2.0)[15]. It was used the experimental equilibrium geometry, in which SF₆ is an octahedron with central S nucleus, external F nucleus and $R_{S-F} = 1.5605 \text{ \AA}$ [16]. The nuclear g_F value was taken to be 5.26 [17].

It is important to remark that the basis set requirements for obtaining molecular coefficients concerning hyperfine interactions with a given accuracy are usually different from those required in energy calculations with the same accuracy. The values of the coefficients are not bound and so there is no analogy in the application of the variational principle.

The basis sets were optimized at the Hartree-Fock level. For the S atom the following basis were considered: the STO-3G* that includes polarization functions [18]; the DZP (Dunning), which is obtained by adding a single set of

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polarization functions (p-functions for hydrogen and d-functions for heavy atoms) to a Double Zeta Basis [19]; and the TZVP (DFT), which is a local spin density basis set that supports S and F atomic numbers [20].

For the F atom we have also used the 6-31++G** basis sets which adds a diffuse (s,p) shell to elements from Li to Cl [21]. The DZP + Diffuse (Dunning) basis sets [19] supports also the atomic number of fluorine but not the sulfur one.

It has been proved that the use of rotational London orbitals is fundamental for obtaining a suitable basis set convergence [9].

The way the orbital connection is defined establishes the correspondence among the orbitals and the values of the perturbation strength. Molecular properties are, in principle, independent of the choice of the orbital connection adopted for the calculation of second order molecular properties. Nevertheless, that choice affects the contributions among the various terms of a given molecular property, like the diamagnetic and paramagnetic contributions to the nuclear magnetic shielding.

It has been shown [22] that only the natural connection enables the obtention of physically well defined contributions for nuclear magnetic shielding. So, we have adopted this approach in our calculations. This is an important issue since we have evaluated the correction due to Thomas precession to the electronic contribution to spin-rotation constants by using Equation (5), which correction only affects the diamagnetic contribution.

To calculate the shielding constants, we have used also the Dalton program, as well as the London atomic orbitals and the natural connection. We were restricted to the HF level since a second-order Møller–Plesset perturbation level [23] (MP2), or a density functional theory (DFT), calculation would disable the use of London orbitals.

The calculations of the spin-rotation constants, for which we have more accurate experimental results, suggest that TZVP(DFT) basis set for S and F nuclei is the more suitable basis for the calculation of magnetic properties. So, we have also used this basis to obtain the shielding constants independently of the spin-rotation constants. A discussion concerning the relation between the values obtained for both constants is presented at the end of Section 4.2.

In the case of the highly symmetric SF₆ molecule (O_h point group), the identical six outside nuclei imposes symmetry conditions which can be adequately treated by the methods of group theory. This approach allows the direct obtention of very simple expressions relating the coefficients of the hyperfine hamiltonian. However, we could not impose *a priori* such high symmetry conditions in the Dalton program we have used. So, we have introduced the highest

symmetry allowed and we have adequately treated the obtained results.

4 Results and discussion

4.1 Spin-rotation constants

A first determination of $|c_a|$ was obtained by Crapo and Flynn [24] from a molecular beam magnetic resonance (MBMR) nuclear moment spectrum. A more detailed study of the rotational magnetic moment spectrum of $^{32}\text{SF}_6$ by the MBMR method, reported by Ozier, Yi and Ramsey [17], produced the experimental value $c_a = -5.27 \pm 0.40$ kHz. The sign of c_a was determined in that work from the relationship between the spin-rotation and the nuclear shielding tensor [25].

The development of the saturation absorption spectroscopy technique has led to results with an increased precision, not only for c_a but also for the tensorial spin rotation tensorial constant c_d . The more precise results obtained with this technique, to our knowledge, are $c_a = -5.140 \pm 0.010$ kHz [3] and $c_d = -4.600 \pm 0.010$ kHz [26]. They will be taken as standard for comparison with our theoretical results due to their high degree of accuracy.

Neglecting the correction due to the Thomas precession in Equation (3), the nuclear contribution to the scalar and tensorial spin-rotation constants are:

$$c_a^n = 4.314 \text{ kHz} \text{ and } c_d^n = 3.783 \text{ kHz} .$$

The correction due to Thomas precession in the nuclear coefficients was calculated by introducing the corrective factor γ_N^T given by Equation (9). We have obtained the following results:

$$c_{a,T}^n = 4.051 \text{ kHz} \text{ and } c_{d,T}^n = 3.388 \text{ kHz}.$$

The corrections due to the Thomas precession in the electronic coefficients were calculated by multiplying the diamagnetic contributions c_a^{ed} and c_d^{ed} , obtained without correction from the Dalton program, by the γ_N^T factor, i. e.,

$$c_{a,T}^{\text{ed}} = \gamma_N^T c_a^{\text{ed}} \text{ and } c_{d,T}^{\text{ed}} = \gamma_N^T c_d^{\text{ed}}. \quad (27)$$

The electronic contributions are the sum of the diamagnetic and paramagnetic contributions.

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The values obtained for the diamagnetic and paramagnetic electronic contributions to the spin-rotation constants, using the adopted basis sets are listed in Table 1, where the subscript “T” means that the correction due to the Thomas precession was taken into account.

In Table 2, we provide the results obtained in this work for the scalar ($c_{a,T}$) and tensorial ($c_{d,T}$) spin-rotation constants with Thomas precession correction. Note that the sign of the electronic correction to the spin-rotation constants due to the Thomas precession is opposite to that of the corresponding nuclear correction.

In Fig. 1, we plot the relative difference, for the scalar and tensorial spin-rotation constants, between the experimental values obtained by Chardonnet and Bordé [3,26] and the results obtained in this work, with ($\Delta c_{a,T}$, $\Delta c_{d,T}$) and without (Δc_a , Δc_d) the Thomas precession correction, where $\Delta c_x = (c_{Exp} - c_x)/c_{Exp}$.

We observe that the theoretical values calculated with the TZVP basis set are the ones that most agree with the experimental results. Furthermore, among this set of values, the ones that incorporate the Thomas precession correction ($\Delta c_{a,T} \simeq 15\%$, $\Delta c_{d,T} \simeq 11\%$) are more close to the experimental values, than the remaining ones ($\Delta c_a = \simeq 16\%$ and $\Delta c_d = 15\%$). Thus, we conclude that the use of the Thomas precession correction improves the comparison between theoretical and experimental values of about 1% in the case of the scalar constant and 4% in the case of the tensorial constant; it means a correction slightly greater than 100Hz for the tensorial contribution.

4.2 Shielding constants

The value of the diamagnetic part of the molecular shielding constant is approximately constant for a given atom from one molecule to another because the chemical environment does not affect this constant. The largest contribution is given by the inner shell electrons. For example, in what concerns the theoretical values obtained for ^{19}F , we have for the F_2 molecule $\sigma^d = 529.5$ ppm, and for the HF molecule $\sigma^d = 492.4$ ppm [27]. We have obtained in this work $\sigma^d = 582.3$ ppm for the SF_6 molecule.

Experimental values for the paramagnetic part of the molecular shielding constant have been early determined and discussed by Mohanty [28] using Sunney and Daas theory [29] and a generalization of the Ramsey’s formula that relates the paramagnetic part of the shielding constant and the spin-rotational constant. The value obtained was -615 ± 26 ppm. By using the same relationship, Ozier, Yi and Ramsey [17] have evaluated the paramagnetic part of the shielding constant from their experimental determination of the spin-rotation

constant obtained by the molecular beam resonance method. These authors obtained the value -575 ± 66 ppm.

Unlike the case of the F_2 molecule (and other similar molecules discussed in [30]) there is no antishielding for the SF_6 molecule. We have obtained the value $\sigma^P = -416.9$ ppm for the fluorine shielding paramagnetic contribution. **This value may be compared with the value for the scalar contribution to the paramagnetic spin-rotation constant obtained with the same basis set, $c_a^{ep} = -6.5207$ KHz (see Table 1). The evaluation of $\sigma^P/c_a^{ep} = 63.93 \times 10^{-3}$ ppm/Hz shows that the Equations (23) and (24) are satisfied with an accuracy of 0.3 %.**

5 Conclusions

We have obtained by *ab initio* methods the values for the scalar and tensorial spin rotation constants of the spherical type SF_6 molecule. The electronic contribution to these constants had only been previously evaluated through the calculation of the difference between the experimental value and the nuclear component, which is exactly obtained from the molecular constants [26].

The basis sets constructed from density functional theory have proved to be the most suitable for these kind of calculations. The use of rotational London orbitals is also crucial to obtain a good convergence.

As discussed by Ramsey, there is a non-negligible correction due to a relativistic Thomas precession resulting from the acceleration of the nuclei. We have evaluated this correction in the framework of the rigid rotor approximation, as we are not taking into account molecular vibration in this work. It has been shown that the introduction of this correction is more significant for the tensorial contribution and improves its comparison with experimental values to a relative difference of 4%.

We have also calculated the diamagnetic and the paramagnetic components of the shielding tensor and compared them with experimental results from previous works. The relationship between the paramagnetic component of the shielding tensor and the spin-rotation tensor has been discussed for spherical tops.

The extension of these calculations beyond the Hartree-Fock level and the inclusion of vibrational effects are the essential tools to improve the calculated results.

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Table 1

Diamagnetic and paramagnetic electronic contributions to the scalar and tensorial spin-rotation constants (KHz). The subscript “T” means that the correction due to the Thomas precession was taken into account.

S and F basis sets	c_a^{ed}	$c_{a,T}^{ed}$	c_d^{ed}	$c_{d,T}^{ed}$	c_a^{ep}	c_d^{ep}
STO-3G, 6-31++G**	-2.334	-2.103	-2.791	-2.514	-5.9006	-4.481
STO-3G, DZP+Diffuse	-1.611	-1.452	-1.831	-1.650	-6.6301	-5.353
DZP, DZP+Diffuse	-2.224	-2.004	-2.663	-2.399	-6.2086	-4.920
TZVP (DFT), TZVP (DFT)	-2.117	-1.907	-2.332	-2.101	-6.5207	-5.382

Table 2

Scalar ($c_{a,T}$) and tensorial ($c_{d,T}$) spin-rotation constants with Thomas precession correction (in KHz) calculated in this work with several basis sets.

S and F basis sets	$c_{a,T}$	$c_{d,T}$
STO-3G, 6-31++G**	-3.953	-3.617
STO-3G, DZP+Diffuse	-4.031	-3.614
DZP, DZP+Diffuse	-4.161	-3.931
TZVP (DFT), TZVP (DFT)	-4.377	-4.095

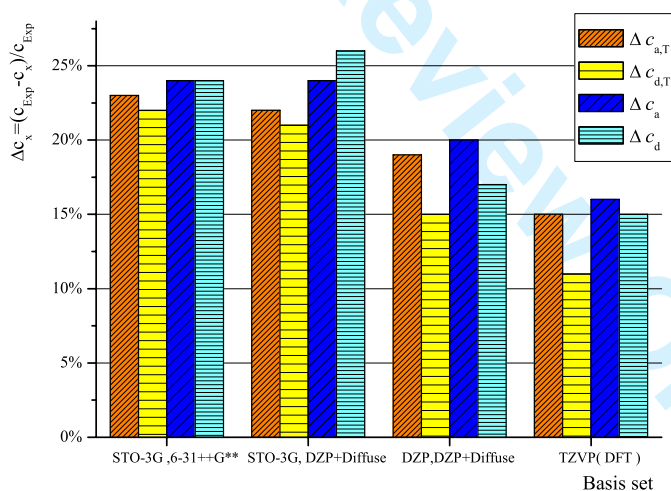


Fig. 1. Relative difference, for the scalar and tensorial spin-rotation constants, between the experimental values obtained by Chardonnet and Bordé [3,26] and the results obtained in this work, with ($\Delta c_{a,T}$, $\Delta c_{d,T}$) and without (Δc_a , Δc_d) the Thomas precession correction.

