

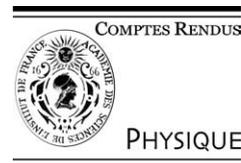


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Gas phase molecular spectroscopy/Spectroscopie moléculaire en phase gazeuse

The spin-vibration hyperfine interaction in the ν_3 band of $^{189}\text{OsO}_4$ and $^{187}\text{OsO}_4$: a calculable example in high-resolution molecular spectroscopy

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Presented by Guy Laval

Abstract

Osmium tetroxide offers the beautiful example of a central particle, the osmium nucleus, with several possible spin values (1/2 for ^{187}Os and 3/2 for ^{189}Os), interacting with the very symmetric and well-defined electromagnetic environment created by a tetrahedron of spinless oxygen nuclei. Among other nuclear hyperfine interactions, the magnetic field generated by the vibrations of these oxygen nuclei orientates this central spin. To study specifically this spin-vibration interaction, the magnetic dipole contributions to the hyperfine structures observed in the ν_3 band of $^{189}\text{OsO}_4$ and $^{187}\text{OsO}_4$ have been analyzed in detail. Besides the spin-rotation constants already deduced in a previous paper, we have obtained the spin-vibration constant, A , and a small change of the spin-rotation constant δc_a in the upper vibrational level. We have verified the speculated relation $A = \zeta_3 c_a$ at the 1% level (ζ_3 is the Coriolis coupling constant, which multiplies the internal vibrational angular momentum to turn it into a physical angular momentum comparable to the pure rotation angular momentum). Starting from first principles, we have rederived the expressions of the magnetic dipole constants for any semi-rigid polyatomic molecule. When these are applied to OsO_4 , they justify the previous approximate relationship between A and c_a and give values for the correction terms which account for the 1% difference. **To cite this article:** C. Chardonnet et al., *C. R. Physique 5 (2004)*.

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Résumé

L'interaction hyperfine spin-vibration dans la bande ν_3 de $^{189}\text{OsO}_4$ et de $^{187}\text{OsO}_4$: un exemple calculable en spectroscopie moléculaire à haute résolution. Le tétr oxyde d' osmium nous offre le bel exemple d' une molécule pour laquelle la particule centrale, le noyau d' osmium, dont le spin peut prendre plusieurs valeurs (1/2 pour ^{187}Os et 3/2 pour ^{189}Os), interagit avec l' environnement électromagnétique très symétrique et très bien défini, créé par un tétraèdre de noyaux d' oxygène sans spin. Parmi d' autres interactions hyperfines nucléaires, le champ magnétique engendré par le mouvement de vibration de ces noyaux d' oxygène contribue à orienter le spin central. Pour étudier spécifiquement cette interaction spin-vibration, les contributions dipolaires magnétiques aux structures hyperfines observées dans la bande de vibration ν_3 de $^{189}\text{OsO}_4$ et $^{187}\text{OsO}_4$ ont été analysées en détail. En plus des constantes de spin-rotation c_a , déjà déduites dans un article antérieur, nous avons obtenu pour chaque espèce isotopique la constante de spin-vibration, A , et la valeur d' une petite variation δc_a de la constante de spin-rotation dans l' état vibrationnel supérieur. Nous avons vérifié la relation conjecturée $A = \zeta_3 c_a$ au niveau de 1 % (ζ_3 est la constante de couplage de Coriolis, qui multiplie le moment angulaire vibrationnel interne pour en faire un moment angulaire physique comparable au moment angulaire de rotation pure). En partant des premiers principes, nous avons recalculé les expressions des constantes dipolaires magnétiques pour toute molécule polyatomique semi-rigide. Quand ces expressions

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sont appliquées à la molécule OsO_4 , elles justifient la relation approchée qui précède entre A et c_a et fournissent des valeurs pour les termes de correction qui rendent compte de la différence de 1 %. **Pour citer cet article : C. Chardonnet et al., C. R. Physique 5 (2004).**

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Keywords: Rovibrational spectroscopy; Magnetic hyperfine structure; Spin-rotation; Spin-vibration; Contact transformation

Mots-clés : Spectroscopie rovibrationnelle ; Structure hyperfine magnétique ; Spin-rotation ; Spin-vibration ; Transformation de contact

1. Introduction

Thanks to non-linear spectroscopic methods (saturation spectroscopy) invented 35 years ago [1], ultra-high resolution molecular spectroscopy is now currently performed with a linewidth of about 1 kHz. This corresponds to a resolving power $\approx 3 \times 10^{10}$ in the 8–12 μm spectral region, in which our spectrometer operates in Villeteuse [2–4]. This resolution is perfectly well-adapted to the observation of the magnetic hyperfine interactions in the rovibrational spectrum of most molecules. Although these interactions are very tiny, they constitute a sensitive probe of the internal dynamics of the molecule. The resolution and the accuracy achieved in the measurement of these interactions open the possibility of a stringent comparison between experiment and theory. This paper follows two earlier ones which present the experimental observations of hyperfine structures in $^{187}\text{OsO}_4$ and $^{189}\text{OsO}_4$ and the analysis of these interactions. This third paper demonstrates a remarkable agreement between a simple theoretical model and our experimental observations.

In a first paper [5], referred to as paper I, we have presented a general introduction to the hyperfine problem in the ν_3 band of $^{189}\text{OsO}_4$ and $^{187}\text{OsO}_4$. The relationships between the experimental splittings and the hyperfine constants (spin-rotation, spin-vibration and quadrupolar coupling constants in both rovibrational levels) have been established. The observation of crossover resonances in saturated absorption gave rise to an independent determination of the hyperfine constants in each vibrational level. As an illustration, we have derived the spin-rotation constants and obtained $^{189}c_a = -21.6891(33)$ kHz and $^{187}c_a = -6.379(20)$ kHz.

In a second paper [6], referred to as paper II, we have focused our attention on the electric quadrupole interaction in $^{189}\text{OsO}_4$. Although, by symmetry, this molecule should not present any quadrupolar structure if it behaved as a rigid rotor, we were able to observe two main contributions, due to the centrifugal distortion and to the vibration and also a weaker one, due to the Coriolis forces. In order to describe correctly the observed structures, we have developed a systematic method for the perturbative treatment of the quadrupolar problem, valid for any semi-rigid molecule. Then, the Hamiltonian was symmetrized using the algebra of the symmetry group of the molecule, ${}^L\text{O}(3) \times T_d$ in order to calculate the matrix elements. The whole procedure enabled us to establish a connection between the quadrupolar constants which are deduced from experiment, and a set of molecular constants, some of which are already known from other spectroscopic works, some others are unknown such as a set of force constants which depend on the shape of the molecular potential. Unfortunately, the number of unknown molecular constants involved in the description of the ‘experimental’ quadrupolar constants was too high and prevented us from any stringent test of the validity of our description of the quadrupolar problem.

In the present paper, we follow the same general idea with the magnetic dipolar problem in $^{189}\text{OsO}_4$ and $^{187}\text{OsO}_4$. In Section 2, we derive the magnetic dipole constants in the upper vibrational state from the experimental data since ground-state spin-rotation constants were already obtained in paper I. In Section 3, starting from first principles, we recall the expression of the magnetic dipolar Hamiltonian. We obtain it by quantization of the classical Hamiltonian which can be derived for any particle in classical electrodynamics. Then, we obtain the magnetic dipole Hamiltonian for any semi-rigid molecule and we express the magnetic constants in terms of elementary molecular constants. Some simplifications of the Hamiltonian based on physical considerations enable us to reduce the number of unknown terms in these expressions and a real comparison between the experimental constants and the values deduced from the theoretical calculations is possible by contrast with the quadrupolar problem. In Section 4, we apply this study to the case of the ν_3 band of $^{189}\text{OsO}_4$ and $^{187}\text{OsO}_4$. For both molecules, we obtain a relation $A = \zeta_3 c_a + w$, where w is completely calculable except for the unknown sign of a parameter which distinguishes between the two F_2 modes of vibration, ν_3 and ν_4 . It is remarkable that the experiment lifts this ambiguity in favor of the mode which is much more likely to be the high frequency mode ν_3 .

2. Determination of the magnetic dipole constants in the upper vibrational level of $^{189}\text{OsO}_4$ and $^{187}\text{OsO}_4$

We have shown in paper I that the hyperfine structures in the ν_3 band of $^{187}\text{Os}^{16}\text{O}_4$ and of $^{189}\text{Os}^{16}\text{O}_4$ appear respectively as two and four main lines identified by $X = F - J = F' - J'$ where $\mathbf{F} = \mathbf{J} + \mathbf{I}$ is the total angular momentum, J , F and J' , F'

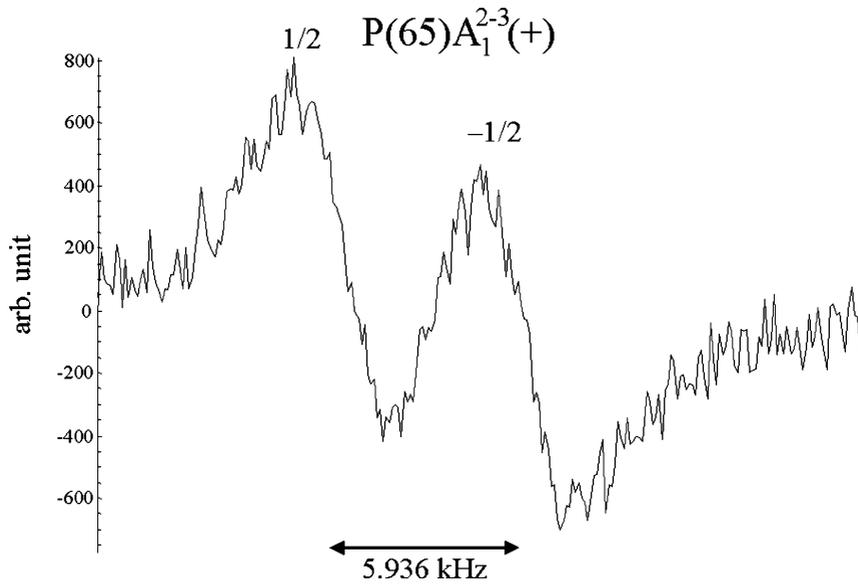


Fig. 1. Spectrum of the P(65) $A_1^{2-3}(+)$ line of $^{187}\text{OsO}_4$, located at -15.260 MHz from the P(18) laser line of the natural CO_2 . The half-width at half-maximum (HWHM) is 2.77 kHz. The magnetic doublet associated to the spin $1/2$ of ^{187}Os is apparent. The rovibrational identification has required mixing of two states due to tensorial interactions. This has no influence on the hyperfine interactions which are essentially scalar. The natural mixture of OsO_4 used here contains 1.64% of $^{187}\text{OsO}_4$. 2sec/point. Uncertainty of the splitting: 50 Hz.

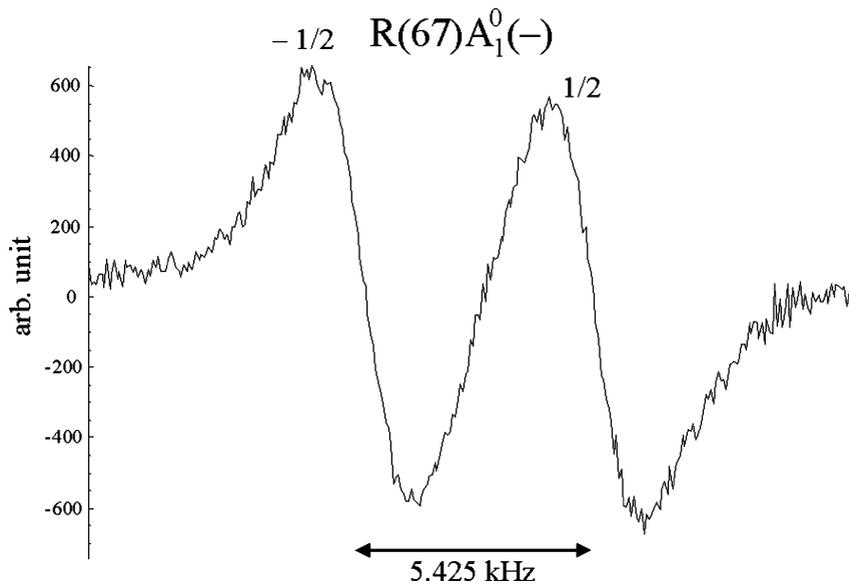


Fig. 2. Spectrum of the R(67) $A_1^0(-)$ line of $^{187}\text{OsO}_4$, located at -1.846 MHz from the R(22) laser line of the natural CO_2 . HWHM = 1.88 kHz. The better signal-to-noise ratio is due to the enriched (at 99%) sample of $^{187}\text{OsO}_4$. 1 sec/point. Uncertainty of the splitting: 13 Hz.

are the quantum numbers in the ground and upper vibrational states, respectively. The spin of ^{187}Os is $I = 1/2$ and, for ^{189}Os , $I = 3/2$. We will keep consistent notations with those introduced in Section III.1 of paper I. The transition frequency of the line identified by X is noted $\Delta E(X)$. Figs. 1–4 give a few examples of hyperfine structures of these two isotopic species. In the case of $^{189}\text{OsO}_4$, the precision on the relative intensities of the hyperfine components, which are mainly proportional to the Zeeman degeneracy, $2F + 1$, was high enough to enable a direct identification of each of these. Eqs. (10) and (11a) of paper I, valid respectively for $^{187}\text{OsO}_4$ and for $^{189}\text{OsO}_4$, can be re-written in the form:

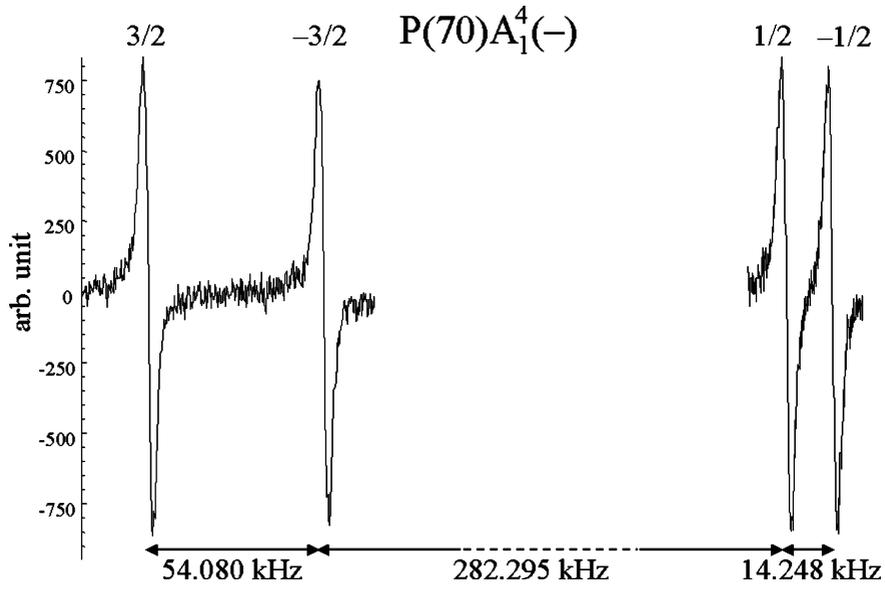


Fig. 3. Spectrum of the P(70) $A_1^4(-)$ line of $^{189}\text{OsO}_4$, located at +149.262 MHz from the P(20) laser line of the natural CO_2 . HWHM = 2.33 kHz. The natural mixture of OsO_4 used here contains 16.1% of $^{189}\text{OsO}_4$. 1 sec/point. Uncertainties of the splittings: from 13 to 20 Hz.

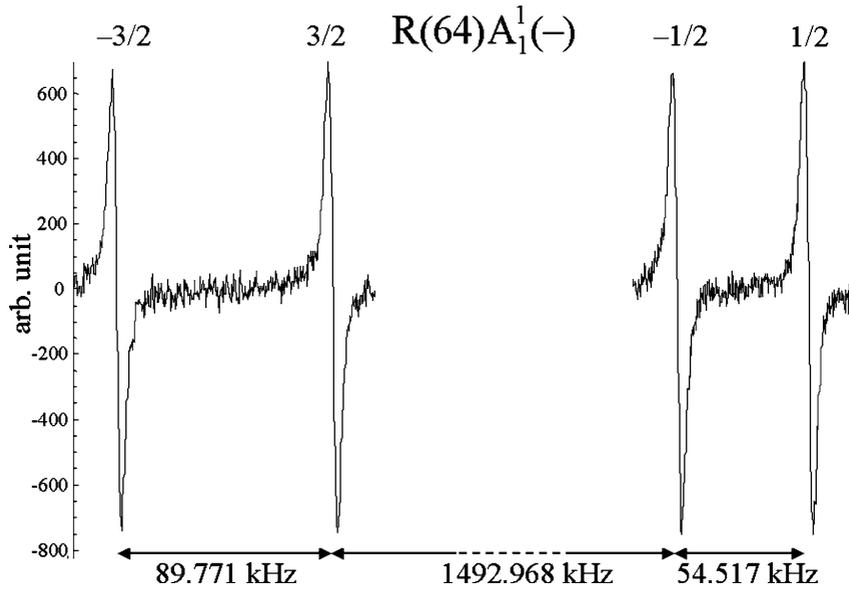


Fig. 4. Spectrum of the R(64) $A_1^1(-)$ line of $^{189}\text{OsO}_4$, located at -146.017 MHz from the R(20) laser line of the natural CO_2 . HWHM = 3.05 kHz. Natural mixture of OsO_4 . 1 sec/point. Uncertainty of the splittings: 19 Hz.

for $^{187}\text{OsO}_4$,

$$\Delta E\left(\frac{1}{2}\right) - \Delta E\left(-\frac{1}{2}\right) = -\frac{2J'+1}{2}\Delta c_a - c_a\Delta J, \quad (1)$$

for $^{189}\text{OsO}_4$,

$$\left[\Delta E\left(\frac{3}{2}\right) - \Delta E\left(-\frac{3}{2}\right)\right] - \left[\Delta E\left(\frac{1}{2}\right) - \Delta E\left(-\frac{1}{2}\right)\right] = -(2J'+1)\Delta c_a - 2c_a\Delta J, \quad (2)$$

Table 1
List of experimental values for Δc_a : case of $^{187}\text{OsO}_4$

$^{187}\text{OsO}_4$	
Line label	Δc_a (Hz)
P(65) $A_1^{2-3}(+)$	−6.87(86)
P(58) $A_1^1(+)$	−8.40(57)
P(38) $A_1^2(-)$	−15.23(61)
R(30) $A_1^1(+)$	30.73(67)
R(30) $A_1^1(-)$	30.67(81)
R(49) $A_1^2(-)$	20.95(57)
R(49) $A_1^2(+)$	20.87(56)
R(55) $A_1^0(+)$	17.82(81)
R(67) $A_1^0(-)$	13.93(35)
R(74) $A_1^0(+)$	15.7(13)
R(74) $A_1^0(-)$	17.3(15)
R(80) $A_1^1(+)$	14.38(79)
R(80) $A_1^1(-)$	15.99(81)

Table 2
List of experimental values for Δc_a : case of $^{189}\text{OsO}_4$

$^{189}\text{OsO}_4$	
Line label	Δc_a (Hz)
P(70) $A_1^4(-)$	−25.52(18)
P(63) $A_1^1(-)$	−31.59(25)
P(56) $A_1^2(+)$	−31.91(23)
P(49) $A_1^3(-)$	−34.94(21)
P(49) $A_1^3(+)$	−34.71(21)
R(26) $A_1^0(+)$	121.88(66)
R(26) $A_1^0(-)$	121.66(61)
R(45) $A_1^0(-)$	77.65(29)
R(57) $A_1^0(+)(a)?$	67.90(48)
R(57) $A_1^0(+)(b)?$	68.47(47)
R(64) $A_1^1(+)$	62.29(22)
R(64) $A_1^1(-)$	62.02(21)
R(64) $A_1^2(+)$	61.46(20)
R(76) $A_1^4(+)$	53.78(38)

where Δc_a is given by:

$$\Delta c_a = \delta c_a - A \frac{\Delta J(J + J' + 1) + 2}{2J'(J' + 1)} = \delta c_a + A Q(J, J'). \quad (3)$$

The left-hand sides of Eqs. (1) and (2) involve splittings between hyperfine components which are measured experimentally. Since the spin-rotation constants $^{189}c_a$ and $^{187}c_a$ have been already determined, we obtain experimental data for Δc_a , which are reported in Tables 1 and 2, corresponding to the two isotopic species. Eq. (3) gives the basis of a linear fit to determine the two hyperfine constants δc_a and A for each isotopic species. The results of these linear fits are displayed in Figs. 5 and 6. We obtain:

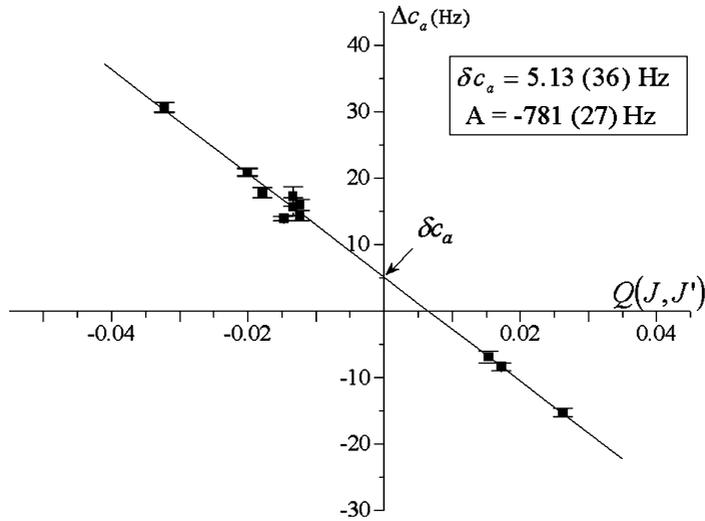


Fig. 5. Linear regression using Eqs. (1) and (3) for the determination of the spin-vibration constant and the change of the spin-rotation constant between the $v_3 = 0$ and the $v_3 = 1$ state in the case of $^{187}\text{OsO}_4$. The error bars are the experimental uncertainties.

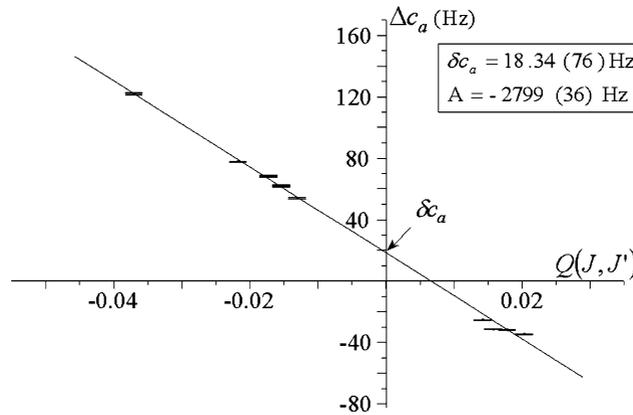


Fig. 6. linear regression as for Fig. 1, using Eqs. (2) and (3) in the case of $^{189}\text{OsO}_4$.

for $^{187}\text{OsO}_4$,

$$\begin{cases} \delta c_a = 5.13(36) \text{ Hz}, & (4a) \\ A = -781(27) \text{ Hz}; & (4b) \end{cases}$$

for $^{189}\text{OsO}_4$,

$$\begin{cases} \delta c_a = 18.34(76) \text{ Hz}, & (5a) \\ A = -2799(36) \text{ Hz}. & (5b) \end{cases}$$

Let us recall the values of the Coriolis coupling constant, ζ_3 , for both isotopic species [7]:

$$\begin{cases} ^{187}\zeta_3 = 0.128165(19), & (6a) \\ ^{189}\zeta_3 = 0.126927(14) & (6b) \end{cases}$$

so that we can verify that:

for $^{187}\text{OsO}_4$,

$$\frac{A}{\zeta_3 c_a} = 0.955(35); \quad (7)$$

for $^{189}\text{OsO}_4$,

$$\frac{A}{\zeta_3 c_a} = 1.017(13). \quad (8)$$

This means that $A_R = \zeta_3 c_a$, which multiplies the rotational part of the spin-vibration interaction, represents the most important contribution to the spin-vibration constant. The remainder of this paper is devoted to the analysis of these hyperfine constants in order to give a physical explanation of such a remarkable relation.

3. Magnetic dipole Hamiltonian from first principles

The purpose of this part is to recall the physical origin of the magnetic dipole Hamiltonian in molecules. For this purpose, we start with a classical approach and derive a simplified classical Hamiltonian for molecules, which is then quantized. The reader will find more general derivations of a full molecular Hamiltonian in the literature [8,9].

3.1. Derivation of the spin-orbit Hamiltonian

We consider a particle of spin \mathbf{s} and of magnetic moment $\boldsymbol{\mu}$ parallel to \mathbf{s} . In its proper frame, the particle probes a magnetic field, \mathbf{B} , and the classical non-relativistic Hamiltonian is:

$$H_{\text{non-rel.}} = -\boldsymbol{\mu} \cdot \mathbf{B}. \quad (9)$$

There is an axial 4-vector, S , which reduces to $S = (0, \mathbf{s})$ in the proper frame of the particle (Thomas–Pauli–Lubanski). If the particle moves at a velocity \mathbf{v} in the laboratory frame, the relativistic Hamiltonian can be written as [10]:

$$H_{\text{rel.}} = -\frac{1}{\gamma} \boldsymbol{\mu} \cdot \mathbf{B}' + \boldsymbol{\omega}_T \cdot \mathbf{s}, \quad (10)$$

where $\gamma = (1 - v^2/c^2)^{-1/2}$, \mathbf{B}' is the magnetic field in the proper frame of the particle and $\boldsymbol{\omega}_T$ is the Thomas precession vector, $\boldsymbol{\omega}_T = -(\gamma^2/(\gamma + 1))(1/c^2)\mathbf{v} \times d\mathbf{v}/dt$. The first term is the interaction energy between the dipole and the magnetic field, the factor $1/\gamma$ is the time dilatation factor in the laboratory frame. The second term has a purely kinematic origin and is a consequence of the fact that the product of two Lorentz transformations is equivalent to a Lorentz transformation and a spatial rotation when the velocity changes its direction.

Let us suppose that the particle has a charge q and is submitted to the Lorentz force created by an electric field \mathbf{E} and a magnetic field \mathbf{B} ; one can show that Eq. (10) takes the following form:

$$H_{\text{rel.}} = -\boldsymbol{\mu} \cdot \left[\left(1 - \frac{qs}{m\mu} \frac{\gamma - 1}{\gamma} \right) \mathbf{B} - \frac{\gamma}{\gamma + 1} \left(1 - \frac{qs}{m\mu} \right) \frac{\mathbf{v}}{c} \cdot \mathbf{B} \frac{\mathbf{v}}{c} - \left(1 - \frac{\gamma}{\gamma + 1} \frac{qs}{m\mu} \right) \frac{\mathbf{v} \times \mathbf{E}}{c^2} \right]. \quad (11)$$

This expression is valid whatever the values of \mathbf{v} , \mathbf{B} and \mathbf{E} . If we assume that the particle is in interaction with the molecular fields and that $\mathbf{v} \ll c$, this Hamiltonian takes a simplified expression:

$$H_{\text{rel.}} = -\boldsymbol{\mu} \cdot \left[\mathbf{B} - \left(1 - \frac{q}{2m} \frac{s}{\mu} \right) \frac{\mathbf{v} \times \mathbf{E}}{c^2} \right] = -\boldsymbol{\mu} \cdot \left[\mathbf{B} - \gamma_i \frac{\mathbf{v} \times \mathbf{E}}{c^2} \right]. \quad (12)$$

The Thomas precession appears only as a correction factor, γ_i , characteristic to the particle i , in front of the motional magnetic field that we will note γ_e for the electron and γ_N for a nucleus N . Expressed in terms of the gyromagnetic factors g and g_N , and the atomic charge Z_N , the mass of the nucleus and the proton, m_N and m_p :

$$\gamma_e = 1 - \frac{1}{g} \approx \frac{1}{2}, \quad (13a)$$

$$\gamma_N = 1 - \frac{Z_N m_p}{g_N m_N}. \quad (13b)$$

In particular, we have $\gamma_{^{189}\text{Os}} = 0.072$ and $\gamma_{^{187}\text{Os}} = -2.2$. \mathbf{B} and \mathbf{E} are the molecular fields created by the electrons and the nuclei of the molecule:

$$\mathbf{E}(\mathbf{r}) = \sum_{\alpha} \mathbf{E}_{\alpha} = \sum_{\alpha} \frac{q_{\alpha}}{4\pi\epsilon_0} \frac{\mathbf{r} - \mathbf{r}_{\alpha}}{|\mathbf{r} - \mathbf{r}_{\alpha}|^3}, \quad (14a)$$

$$\mathbf{B}(\mathbf{r}) = \sum_{\alpha} \mathbf{B}_{\alpha} = \sum_{\alpha} \frac{1}{c^2} \mathbf{v}_{\alpha} \times \mathbf{E}_{\alpha} + \frac{\mu_0}{4\pi} \left(\frac{3\boldsymbol{\mu}_{\alpha} \cdot (\mathbf{r} - \mathbf{r}_{\alpha})}{|\mathbf{r} - \mathbf{r}_{\alpha}|^5} (\mathbf{r} - \mathbf{r}_{\alpha}) - \frac{\boldsymbol{\mu}_{\alpha}}{|\mathbf{r} - \mathbf{r}_{\alpha}|^3} + \frac{8\pi}{3} \boldsymbol{\mu}_{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\alpha}) \right). \quad (14b)$$

We can now write a spin-orbit Hamiltonian:

$$\begin{aligned} H_{\text{S.O.}} = & \frac{\mu_0 e}{4\pi} \sum_{\substack{i,j \\ i \neq j}} \boldsymbol{\mu}_i \cdot \left[(\mathbf{v}_j - \gamma_e \mathbf{v}_i) \times \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|^3} \right] - \frac{\mu_0 e}{4\pi} \sum_{i,K} \boldsymbol{\mu}_i \cdot \left[(\mathbf{v}_K - \gamma_e \mathbf{v}_i) \times \frac{Z_K (\mathbf{r}_i - \mathbf{r}_K)}{|\mathbf{r}_i - \mathbf{r}_K|^3} \right] \\ & + \frac{\mu_0 e}{4\pi} \sum_{N,j} \boldsymbol{\mu}_N \cdot \left[(\mathbf{v}_j - \gamma_N \mathbf{v}_N) \times \frac{\mathbf{r}_N - \mathbf{r}_j}{|\mathbf{r}_N - \mathbf{r}_j|^3} \right] - \frac{\mu_0 e}{4\pi} \sum_{\substack{N,K \\ N \neq K}} \boldsymbol{\mu}_N \cdot \left[(\mathbf{v}_K - \gamma_N \mathbf{v}_N) \times \frac{Z_K (\mathbf{r}_N - \mathbf{r}_K)}{|\mathbf{r}_N - \mathbf{r}_K|^3} \right], \end{aligned} \quad (15)$$

where the indices i and j refer to the electrons and the indices N and K to the nuclei N and K . This Hamiltonian can be quantized and symmetrized:

$$\begin{aligned} H_{\text{S.O.}} = & \frac{\mu_0 e}{4\pi} \left\{ -g\mu_B \sum_{\substack{i,j \\ i \neq j}} \mathbf{s}_i \cdot \left[\left(\frac{\boldsymbol{\Pi}_j}{m_e} - \gamma_e \frac{\boldsymbol{\Pi}_i}{m_e} \right) \times \frac{\mathbf{R}_{ij}}{R_{ij}^3} \right] + g\mu_B \sum_{i,K} \mathbf{s}_i \cdot \left[\left(\frac{\boldsymbol{\Pi}_K}{m_K} - \gamma_e \frac{\boldsymbol{\Pi}_i}{m_e} \right) \times \frac{Z_K \mathbf{R}_{iK}}{R_{iK}^3} \right] \right. \\ & + \mu_n \sum_{N,j} g_N \mathbf{I}_N \cdot \left[\left(\frac{\boldsymbol{\Pi}_j}{m_e} - \gamma_N \frac{\boldsymbol{\Pi}_N}{m_N} \right) \times \frac{\mathbf{R}_{Nj}}{R_{Nj}^3} \right] \\ & \left. - \mu_n \sum_{\substack{N,K \\ N \neq K}} g_N \mathbf{I}_N \cdot \left[\left(\frac{\boldsymbol{\Pi}_K}{m_K} - \gamma_N \frac{\boldsymbol{\Pi}_N}{m_N} \right) \times \frac{Z_K \mathbf{R}_{NK}}{R_{NK}^3} \right] \right\}_{\text{symm}}. \end{aligned} \quad (16)$$

We have introduced the operators \mathbf{s}_i , \mathbf{I}_N ,¹ \mathbf{R}_α , $\boldsymbol{\Pi}_\alpha$ for the electronic spins, the nuclear spins, the position-vector ($\mathbf{R}_{\alpha\beta} = \mathbf{R}_\alpha - \mathbf{R}_\beta$) and the canonical momentum in the laboratory frame for the particle α . This last operator is related to the usual momentum of the particle by the relation $\boldsymbol{\Pi}_\alpha = \mathbf{P}_\alpha - q_\alpha \mathbf{A}_\alpha(\mathbf{R}_\alpha)$ where $\mathbf{A}_\alpha(\mathbf{R}_\alpha)$ is the potential-vector created by the other particles (electrons + nuclei) at the position of the particle α . Now, in order to be able to calculate the various contributions of this Hamiltonian, we need to introduce the relevant coordinates expressed in the molecular frame. Since the procedure is canonical, we shall just give the result. The Hamiltonian splits into two parts, the nuclear spin-orbit and the electronic spin-orbit terms:

$$\begin{aligned} H_{\text{S.O.}}^n = & \frac{\mu_0 e}{4\pi} \left\{ -\mu_n \sum_{\substack{N,K \\ N \neq K}} g_N \mathbf{I}_N \cdot I''^{1/2} \left[\left[\left(\frac{\vec{\ell}_{K\lambda}}{\sqrt{m_K}} - \gamma_N \frac{\vec{\ell}_{N\lambda}}{\sqrt{m_N}} \right) P_\lambda \right. \right. \right. \\ & \left. \left. - (\mathbf{r}_K^0 - \gamma_N \mathbf{r}_N^0) \times (\mathbf{I}''^{-1} \cdot \mathbf{N}) \right] \times \frac{Z_K \mathbf{r}_{NK}}{r_{NK}^3} \right] I''^{-1/2} \\ & \left. + \mu_n \sum_{N,j} g_N \mathbf{I}_N \cdot I''^{1/2} \left[\left[\frac{\mathbf{p}_i}{m_e} - \gamma_N \left(\frac{\vec{\ell}_{N\lambda}}{\sqrt{m_N}} P_\lambda - \mathbf{r}_N^0 \times (\mathbf{I}''^{-1} \cdot \mathbf{N}) \right) \right] \times \frac{\mathbf{r}_{Ni}}{r_{Ni}^3} \right] I''^{-1/2} \right\}_{\text{symm}}, \end{aligned} \quad (17a)$$

$$\begin{aligned} H_{\text{S.O.}}^e = & \frac{\mu_0 e}{4\pi} \left\{ -g\mu_B \sum_{\substack{i,j \\ i \neq j}} \mathbf{s}_i \cdot \left[\left(\frac{\mathbf{p}_j}{m_e} - \gamma_e \frac{\mathbf{p}_i}{m_e} \right) \times \frac{\mathbf{r}_{ij}}{r_{ij}^3} \right] \right. \\ & \left. + g\mu_B \sum_{i,K} \mathbf{s}_i \cdot I''^{1/2} \left[\left(\frac{\vec{\ell}_{K\lambda}}{\sqrt{m_K}} P_\lambda - \mathbf{r}_K^0 \times (\mathbf{I}''^{-1} \cdot \mathbf{N}) - \gamma_e \frac{\mathbf{p}_i}{m_e} \right) \times \frac{Z_K \mathbf{r}_{iK}}{r_{iK}^3} \right] I''^{-1/2} \right\}_{\text{symm}}. \end{aligned} \quad (17b)$$

λ corresponds to a normal vibrational mode and a sum over this index is assumed. Most of the new quantities introduced here correspond to standard notations. $I''^{\pm 1/2}$ involves the determinant of the matrix \mathbf{I}'' and comes from the Jacobian related to the change of variables. It does not commute with P_λ . The Hamiltonian involving the electronic spins cancels to first order when the total electronic spin is zero. Since we are only interested in the hyperfine terms we shall consider only the nuclear spin-orbit Hamiltonian which can be rewritten as a sum of 5 terms:

$$H_{\text{S.O.}}^n = H_{\text{SR}}^n + H_{\text{SR}}^e + H_{\text{SV}}^n + H_{\text{SV}}^e + H_{\text{S.O.}}^{\text{nd}} \quad (18)$$

with the following expressions:

¹ Note that, for example, $\boldsymbol{\mu}_N = g_N \mu_n \mathbf{I}_N$ implies that, as for the other spins, \mathbf{I}_N is dimensionless and expressed in units of \hbar .

$$H_{\text{SR}}^{\text{n}} = \frac{\mu_0 e}{4\pi} \left\{ \mu_n \sum_{\substack{N,K \\ N \neq K}} g_N \mathbf{I}_N \cdot I''^{1/2} \left[[(\mathbf{r}_K^0 - \gamma_N \mathbf{r}_N^0) \times (\mathbf{I}''^{-1} \cdot (\mathbf{J} - \mathbf{G}) \hbar)] \times \frac{Z_K \mathbf{r}_{NK}}{r_{NK}^3} \right] I''^{-1/2} \right\}_{\text{symm}}, \quad (19)$$

$$H_{\text{SR}}^{\text{e}} = \frac{\mu_0 \mu_n e}{4\pi} \left\{ \sum_{i,N} g_N \mathbf{I}_N \cdot I''^{1/2} \left[[\gamma_N \mathbf{r}_N^0 \times (\mathbf{I}''^{-1} \cdot (\mathbf{J} - \mathbf{G}) \hbar)] \times \frac{\mathbf{r}_{Ni}}{r_{Ni}^3} \right] I''^{-1/2} \right\}_{\text{symm}}, \quad (20)$$

$$H_{\text{SV}}^{\text{n}} = -\frac{\mu_0 \mu_n e}{4\pi} \left\{ \sum_{\substack{N,K \\ N \neq K}} g_N \mathbf{I}_N \cdot I''^{1/2} \left[\left[\left(\frac{\bar{\ell}_{K\lambda}}{\sqrt{m_K}} - \gamma_N \frac{\bar{\ell}_{N\lambda}}{\sqrt{m_N}} \right) P_\lambda \right] \times \frac{Z_K \mathbf{r}_{NK}}{r_{NK}^3} \right] I''^{-1/2} \right\}_{\text{symm}}, \quad (21)$$

$$H_{\text{SV}}^{\text{e}} = -\frac{\mu_0 \mu_n e}{4\pi} \left\{ \sum_{N,i} g_N \mathbf{I}_N \cdot I''^{1/2} \left[\gamma_N \frac{\bar{\ell}_{N\lambda}}{\sqrt{m_N}} P_\lambda \times \frac{\mathbf{r}_{Ni}}{r_{Ni}^3} \right] I''^{-1/2} \right\}_{\text{symm}}, \quad (22)$$

$$H_{\text{S.O.}}^{\text{nd}} = \frac{\mu_0 \mu_n e}{4\pi} \left\{ \sum_{i,N} g_N \mathbf{I}_N \cdot \frac{\mathbf{p}_i \times \mathbf{r}_{Ni}}{m_e r_{Ni}^3} - \sum_{\substack{N,K \\ N \neq K}} g_N \mathbf{I}_N \cdot \left[[(\mathbf{r}_K^0 - \gamma_N \mathbf{r}_N^0) \times (\mathbf{I}''^{-1} \cdot \mathbf{L})] \times \frac{Z_K \mathbf{r}_{NK}}{r_{NK}^3} \right] \right. \\ \left. - \sum_{i,N} g_N \mathbf{I}_N \cdot \left[[\gamma_N \mathbf{r}_N^0 \times (\mathbf{I}''^{-1} \cdot \mathbf{L})] \times \frac{\mathbf{r}_{Ni}}{r_{Ni}^3} \right] \right\}_{\text{symm}}. \quad (23)$$

The four first terms of $H_{\text{S.O.}}^{\text{nd}}$ will give a contribution to first order to the spin-rotation Hamiltonians (index SR) of nuclear (n) or electronic (e) origin and to the spin-vibration Hamiltonians (index SV). One can note that $\mathbf{I}''^{-1} \cdot (\mathbf{J} - \mathbf{G}) \hbar$ represents,² in a $^1\Sigma_g$ electronic state, the operator associated with nuclear rotation. Finally, the last term gives a non-zero contribution only by breaking the Born–Oppenheimer approximation. In order to obtain a contribution to the spin-rotation interaction, we need to couple the term to an orbital term linear with $\mathbf{J} - \mathbf{G}$. The only possible term is:

$$H_{\text{orb}}^{\text{nd}} = -\frac{1}{2} (\mathbf{J} - \mathbf{G}) \cdot \boldsymbol{\mu} \cdot \mathbf{L} + \mathbf{L} \cdot \boldsymbol{\mu} \cdot (\mathbf{J} - \mathbf{G}) \hbar. \quad (24)$$

It is noticeable that there is no other orbital term which can generate a second-order contribution to the spin-vibration interaction except this one which depends on \mathbf{G} . The second-order spin-rotation term is, thus, given by:

$$H_{\text{SR}}^{(2)} = -\frac{\mu_0 \mu_n e}{4\pi m_e} \left\{ \sum_N g_N \mathbf{I}_N \cdot \frac{\langle 0 | \mathbf{L}'_N | p \rangle \langle p | \mathbf{L} | 0 \rangle \cdot \boldsymbol{\mu} + \langle p | \mathbf{L}'_N | 0 \rangle \langle 0 | \mathbf{L} | p \rangle \cdot \boldsymbol{\mu}}{V_p - V_0} (\mathbf{J} - \mathbf{G}) \hbar \right\}_{\text{symm}} \quad (25)$$

where $\mathbf{L}'_N = \sum_i (\mathbf{r}_{Ni} \times \mathbf{p}_i) / r_{Ni}^3$. This last term completes Eqs. (21)–(24) which will give the dominant contributions to the spin-rotation and spin-vibration interactions.

3.2. The spin-rotation tensor

The spin-rotation tensor ${}^N\mathbf{C}$ is defined as:

$$H_{\text{SR}} = -\frac{1}{2} \sum_N h (\mathbf{I}_N \cdot {}^N\mathbf{C} \cdot (\mathbf{J} - \mathbf{G}) + (\mathbf{J} - \mathbf{G}) \cdot {}^N\mathbf{C} \cdot \mathbf{I}_N) = -h \left\{ \sum_N \mathbf{I}_N \cdot {}^N\mathbf{C} \cdot (\mathbf{J} - \mathbf{G}) \right\}_{\text{symm}}. \quad (26)$$

This tensor is a constant (expressed in Hz). It will be obtained by considering the nuclei at their equilibrium position in Eqs. (19), (20) and (25). From Eqs. (19), (20), the spin-orbit Hamiltonian to first order can be written as:

$$H_{\text{SR}}^{(1)} = \left\{ \frac{\mu_0 \mu_n e}{4\pi m_e} \sum_{\substack{N,K \\ N \neq K}} g_N \mathbf{I}_N \cdot \left[[\mathbf{r}_K^0 \times ((\mathbf{I}^0)^{-1} \cdot (\mathbf{J} - \mathbf{G}))] \times \frac{Z_K \mathbf{r}_{NK}^0}{r_{NK}^3} \right] \right. \\ \left. - \frac{1}{c^2} \mu_n \sum_N g_N \mathbf{I}_N \cdot \left[[\gamma_N \mathbf{r}_N^0 \times ((\mathbf{I}^0)^{-1} \cdot (\mathbf{J} - \mathbf{G}))] \right] \right. \\ \left. \times \left[\sum_{\substack{K \\ K \neq N}} \frac{Z_K e r_{NK}^0}{4\pi \epsilon_0 r_{NK}^3} - \sum_i \left\langle 0 \left| \frac{e \mathbf{r}_{Ni}^0}{4\pi \epsilon_0 r_{Ni}^3} \right| 0 \right\rangle \right] \right\}_{\text{symm}}, \quad (27)$$

² \mathbf{J} and \mathbf{G} are dimensionless and expressed in units of \hbar .

where the expression which appears in the last brackets has a simple physical meaning. It represents the Coulomb field $\mathbf{E}_{\text{Coul.}}^N$ at the nucleus N created by the other particles of the molecule. The corresponding force, $\mathbf{F}_{\text{Coul.}}^N = Z_N e \mathbf{E}_{\text{Coul.}}^N$, applied on this nucleus is responsible for its rotation as the molecule is considered as a rigid rotor. A classical picture is given by the fundamental law of the dynamics:

$$\mathbf{F}_{\text{Coul.}}^N = m_N \boldsymbol{\omega} \times (\boldsymbol{\omega} \times \mathbf{r}_N^0),$$

where $\boldsymbol{\omega}$ represents the angular velocity expressed by $(\mathbf{I}^0)^{-1} \cdot (\mathbf{J} - \mathbf{G})$. Thus, it turns out that the corresponding term in the Hamiltonian can be interpreted as a higher-order term in $(\mathbf{I}^0)^{-1} \cdot (\mathbf{J} - \mathbf{G})$ and can be neglected. This is confirmed by a simple calculation of order of magnitude: the ratio between the second and the first term of H_{SR}^1 is of the order of: $4\pi \epsilon_0 m_N \omega^2 r^3 / (Z_N Z_K e^2)$. Since $\omega \approx J \hbar / (M r^2)$, where M is the molecular mass, realistic numerical applications give a ratio of $A_N J^2 / (A_{\text{mol.}}^2 Z_N Z_K) \times 10^{-4}$ (A_N and $A_{\text{mol.}}$ are the atomic masses of N and the whole molecule, respectively) which is very small if $J \leq 100$, whatever the molecule is. Neglecting this term has two consequences: first, the Thomas precession term disappears, i.e., the acceleration of the nuclei due to the rotation induces a negligible spin precession compared to that due to the magnetic field created by the moving charges in the molecule; second, the first-order spin-rotation Hamiltonian depends only on the nuclear coordinates and is completely calculable. Thus, the expression of the spin-rotation tensor is given by:

$${}^N\mathbf{C} = {}^N\mathbf{C}^{\text{n}} + {}^N\mathbf{C}^{\text{e}}, \quad (28)$$

where the nuclear and electronic spin-rotation tensors are defined by:

$${}^N\mathbf{C}_{\alpha\beta}^{\text{n}} = \frac{\mu_0 \mu_n e}{4\pi} g_N \sum_{K, K \neq N} Z_K \left(\frac{r_{K\alpha}^0 r_{NK\beta}^0 - \mathbf{r}_K^0 \cdot \mathbf{r}_{NK}^0 \delta_{\alpha\beta}}{r_{NK}^0{}^3} \right) \frac{1}{I_{\beta\beta}^0}, \quad (29a)$$

$${}^N\mathbf{C}_{\alpha\beta}^{\text{e}} = \frac{\mu_0 \mu_n e}{4\pi} g_N \sum_{p, p \neq 0} \frac{\langle 0 | L'_{N\alpha} | p \rangle \langle p | L_\beta | 0 \rangle + \langle 0 | L_\beta | p \rangle \langle p | L'_{N\alpha} | 0 \rangle}{V_p - V_0} \frac{1}{m_e I_{\beta\beta}^0}, \quad (29b)$$

where the superscript 0 in $L'_{N\alpha}$ indicates that the nucleus N is taken at its equilibrium position.

3.3. The spin-vibration tensor

The spin-vibration interaction comes from the coupling between the nuclear spins and the angular momentum induced by the vibration. The general form of the associated Hamiltonian is:

$$H_{\text{SV}} = \frac{1}{2} \sum_N \mathbf{I}_N \cdot \sum_\lambda ({}^N\mathbf{v}_\lambda p_\lambda + p_\lambda {}^N\mathbf{v}_\lambda). \quad (30)$$

We develop this expression to second order in q_λ and p_λ :

$$H_{\text{SV}} = \sum_N \mathbf{I}_N \cdot \left[\sum_\lambda {}^N\mathbf{v}_\lambda p_\lambda + \frac{1}{2} \sum_\lambda {}^N\mathbf{w}_{\lambda\mu} (q_\lambda p_\mu + p_\mu q_\lambda) + \dots \right]. \quad (31)$$

This Hamiltonian is actually the sum of H_{SV}^{n} and H_{SV}^{e} given by Eqs. (21) and (22) and it can be re-written as:

$$H_{\text{SV}} = -\frac{\mu_0 \mu_n e}{4\pi} \left\{ \sum_{\substack{N, K \\ N \neq K}} g_N \mathbf{I}_N \cdot \left[P_\lambda \frac{\vec{\ell}_{K\lambda}}{\sqrt{m_K}} \times \frac{Z_K \mathbf{r}_{NK}}{r_{NK}^3} \right] \right. \\ \left. - \sum_N \gamma_N g_N \mathbf{I}_N \cdot \left[P_\lambda \frac{\vec{\ell}_{N\lambda}}{\sqrt{m_N}} \times \left(\sum_{K, K \neq N} \frac{Z_K \mathbf{r}_{NK}}{r_{NK}^3} - \left\langle 0 \left| \sum_i \frac{\mathbf{r}_{Ni}}{r_{Ni}^3} \right| 0 \right\rangle \right) \right] \right\}_{\text{symm}}. \quad (32)$$

As in the case of the spin-rotation interaction, the second contribution involves terms proportional to the Coulomb forces exerted on the nuclei N . These Coulomb forces are responsible for the rotation and the vibration of the nuclei. If we neglect the rotation here, which can only contribute to higher-order terms, we see that the Coulomb force derives from the molecular potential which can be developed versus the normal coordinates:

$$V = V_0 + \frac{1}{2} \sum_\lambda \hbar \omega_\lambda q_\lambda^2 + \hbar c \sum_{\lambda, \mu, \nu} K_{\lambda\mu\nu} q_\lambda q_\mu q_\nu + \dots, \quad (33)$$

where the vibrational pulsation ω_λ is introduced and is related to the ‘vibrational frequency’ – commonly expressed in cm^{-1} and introduced in paper II – by $\omega_\lambda = 2\pi c\omega_\lambda$. Thus the force obtained at the first order in q_λ is:

$${}^N\mathbf{F} = -\nabla_{\mathbf{r}_N} V = -\sum_{\lambda} \hbar\omega_\lambda q_\lambda \nabla_{\mathbf{r}_N} q_\lambda = -\sum_{\lambda} \sqrt{m_N \hbar\omega_\lambda^3} \vec{\ell}_{N\lambda} q_\lambda \quad (34)$$

and the new expression of the spin-vibration Hamiltonian is:

$$\begin{aligned} H_{\text{SV}} = & -\frac{\mu_0\mu_n e}{4\pi} \left\{ \sum_{\substack{N,K \\ N \neq K}} g_N \mathbf{I}_N \cdot \left[\sqrt{\hbar\omega_\lambda} p_\lambda \frac{\vec{\ell}_{K\lambda}}{\sqrt{m_K}} \times \frac{Z_K \mathbf{r}_{NK}}{r_{NK}^3} \right] \right\}_{\text{symm}} \\ & + \frac{\hbar\mu_n}{ec^2} \sum_N \frac{\gamma_N}{Z_N} g_N \mathbf{I}_N \cdot \left[\sum_{\lambda,\mu} \omega_\lambda^2 \vec{\ell}_{N\lambda} \times \vec{\ell}_{N\mu} q_\lambda p_\mu \right], \end{aligned} \quad (35)$$

where the conjugate momentum P_λ has been replaced by the dimensionless one p_λ defined by: $P_\lambda = \sqrt{\hbar\omega_\lambda} p_\lambda$. A simple development versus the normal coordinates leads to the expressions of the tensors ${}^N\mathbf{v}_\lambda$ and ${}^N\mathbf{w}_{\lambda\mu}$:

$${}^N\mathbf{v}_\lambda = -\frac{\mu_0\mu_n g_N e}{4\pi} \sum_{K, K \neq N} \left[\sqrt{\hbar\omega_\lambda} \frac{\vec{\ell}_{K\lambda}}{\sqrt{m_K}} \times \frac{Z_K \mathbf{r}_{NK}^0}{r_{NK}^0{}^3} \right], \quad (36)$$

$$\begin{aligned} {}^N\mathbf{w}_{\lambda\mu} = & \frac{\hbar\mu_0\mu_n g_N e}{4\pi} \sum_{K, K \neq N} \frac{Z_K}{r_{NK}^0{}^3} \left[\frac{\vec{\ell}_{N\lambda}}{\sqrt{m_N}} - \frac{\vec{\ell}_{K\lambda}}{\sqrt{m_K}} - 3 \left(\left(\frac{\vec{\ell}_{N\lambda}}{\sqrt{m_N}} - \frac{\vec{\ell}_{K\lambda}}{\sqrt{m_K}} \right) \cdot \mathbf{r}_{NK}^0 \right) \frac{\mathbf{r}_{NK}^0}{r_{NK}^0{}^2} \right] \times \frac{\vec{\ell}_{K\mu}}{\sqrt{m_K}} \\ & + \frac{\hbar\mu_n \gamma_N g_N}{Z_N ec^2} \omega_\lambda^2 \vec{\ell}_{N\lambda} \times \vec{\ell}_{N\mu}. \end{aligned} \quad (37)$$

In a given vibrational level, the contribution of the first term in Eq. (31) is zero since the operator p_λ is off-diagonal. The first non-zero contribution comes from the second term whose physics is expressed by Eq. (37) of the tensor ${}^N\mathbf{w}_{\lambda\mu}$. The first line comes from the usual interaction between the molecular magnetic field and the nuclear spin while the second line represents the motional terms: it includes in particular the Thomas precession. It is easy to estimate the relative contribution of these two terms as we did in the case of the spin-rotation interaction: the ratio is of the order of $4\pi\epsilon_0\sqrt{m_N m_K} \omega_\lambda^2 r^3 / (Z_N Z_K e^2)$, an expression very similar to that obtained in the case of the rotation except that the rotational frequency is replaced by the vibrational frequency. In the case of a vibration in the 10 μm region, one finds a ratio of the order of $\sqrt{A_N A_K} / (Z_N Z_K)$ which is typically between 0.1 and 1. This means that the motional terms cannot be neglected when the vibration is considered.

3.4. New definition of the spin-vibration tensor

Because the molecular rotation is better represented by the angular momentum $\mathbf{J} - \mathbf{G}$, we have expressed the spin-rotation Hamiltonian with this quantity which appears naturally. However, for an analysis of the hyperfine constants from experimental data, it is preferable to assemble terms having the same signature. Thus, we introduce the spin-vibration-rotation Hamiltonian with the following development:

$$H_{\text{SVR}} = -\left\{ \sum_N \mathbf{I}_N \cdot {}^N\mathbf{C} \cdot \mathbf{J} \right\}_{\text{symm}} + \sum_N \mathbf{I}_N \cdot \left[\sum_{\lambda} {}^N\mathbf{v}_\lambda p_\lambda \right] + \sum_N \mathbf{I}_N \cdot \left[\sum_{\lambda} {}^N\mathbf{v}_{\lambda\mu} \frac{1}{2} (q_\lambda p_\mu + p_\mu q_\lambda) \right] + \dots \quad (38)$$

This expression preserves the spin-rotation tensor as well as the tensor ${}^N\mathbf{v}_\lambda$. We have to define a new spin-vibration tensor by the relation:

$${}^N\mathbf{v}_{\lambda\mu} = {}^N\mathbf{w}_{\lambda\mu} + {}^N\mathbf{C} \cdot \boldsymbol{\zeta}_{\lambda\mu} \quad (39)$$

and we will keep in mind that the second part of this tensor has a rotational origin.

This spin-vibration interaction has been introduced by Uehara and Shimoda [11] and first observed in the hyperfine spectrum of SF_6 in our laboratory [12].

The treatment presented here is applicable to any semi-rigid polyatomic molecule. We will now consider the specific case of OsO_4 .

4. Magnetic dipole constants in Os¹⁶O₄

4.1. The spin-rotation constants in ¹⁸⁹OsO₄ and ¹⁸⁷OsO₄

In Os¹⁶O₄, we have to consider the evolution of a single spin ($I_{189\text{Os}} = 3/2$ and $I_{187\text{Os}} = 1/2$) at the center of a tetrahedron. By symmetry considerations, the spin-rotation tensor defined in Eq. (26), must be a scalar. The spin-rotation Hamiltonian takes the simple form which is immediately symmetrized in the molecular group ${}^{(L)}\text{O}(3) \times T_d$:

$$H_{\text{SR}} = -hc_a \{\mathbf{I} \cdot \mathbf{J}\}_{\text{symm}} = -hc_a \sqrt{3} [\mathbf{I}^{(1,A_1)} \times \{D^{(1,1)} \times I^{(0,1)}\}^{(1,0A_1)}]^{(0,A_1)}. \quad (40)$$

From Eq. (29), we deduce directly the expression of the spin-rotation constant which has a nuclear and an electronic contribution:

$$c_a = c_a^n + c_a^e \quad (41)$$

with

$$c_a^n = {}^{\text{Os}} C_{xx}^n = \frac{\mu_0}{4\pi} \frac{g_{\text{Os}} \mu_n Z_{\text{O}} e}{2\pi m_{\text{O}} r^3}, \quad (42a)$$

$$c_a^e = {}^{\text{Os}} C_{xx}^e = \frac{\mu_0}{4\pi} \frac{3}{16\pi} \frac{g_{\text{Os}} \mu_n Z_{\text{O}} e}{m_e m_{\text{O}} r^3} \times \sum_{p, p \neq 0} \frac{\langle 0 | \sum_i \{(\mathbf{r}_i \times \mathbf{p}_i) / r_i^3\}_x | p \rangle \langle p | L_x | 0 \rangle + \langle 0 | L_x | p \rangle \langle p | \sum_i \{(\mathbf{r}_i \times \mathbf{p}_i) / r_i^3\}_x | 0 \rangle}{V_p - V_0}, \quad (42b)$$

where g_{Os} , Z_{O} , m_{O} , r are respectively the gyromagnetic factor of the nucleus Os, the atomic charge and the mass of the oxygen nucleus and the distance O–Os when the nuclei are at their equilibrium. The value of the momentum of inertia at equilibrium, $I^0 = 8/3 m_{\text{O}} r^2$, has been used. With these expressions, the constants are expressed in Hz.

4.1.1. Numerical applications

One can find on the web [13,14] accurate values for these parameters which will permit us to calculate at least the nuclear contribution to the spin-rotation constant. Using the experimental value, we deduce the electronic contribution.

$$g_{189\text{Os}} = 0.4395533, \quad g_{187\text{Os}} = 0.12930378, \quad m_{\text{O}} = 15.99491463(\text{a.u.})$$

and $r_{\text{O–Os}} = 0.171160(10)$ nm.

One finds:

$${}^{189}c_a^n = 340.37(6) \text{ Hz}, \quad (43a)$$

$${}^{189}c_a^e = -22029.5(33) \text{ Hz} \quad (43b)$$

and

$${}^{187}c_a^n = 100.035(20) \text{ Hz}, \quad (44a)$$

$${}^{187}c_a^e = -6479(20) \text{ Hz}. \quad (44b)$$

We observe that, in both cases, the electronic contribution is the dominant part as it is well known and it illustrates the fact that the spin-rotation interaction is mainly due to a breaking of the Born-Oppenheimer interaction. However, the nuclear contribution is significant considering the accuracy of the experimental data.

4.2. The spin-vibration constants in ¹⁸⁹OsO₄ and ¹⁸⁷OsO₄

We are essentially concerned by the triply degenerate vibration mode ν_3 in OsO₄. Thus, we shall reduce the vibrational degrees of freedom to this particular mode and from the total vibrational angular momentum \mathbf{G} , we build its restriction to ν_3 :

$$\mathbf{G}_3 = \sum_{\sigma, \sigma'} \xi_{3\sigma, 3\sigma'} q_{3\sigma} p_{3\sigma'}. \quad (45)$$

According to the adopted orientation of the representations of the point-group T_d recalled in our paper II, the coordinates of the vectors $\xi_{3\beta, 3\gamma}^\alpha$ verify:

$$\xi_{3\beta, 3\gamma}^\alpha = \xi_{3\varepsilon\alpha\beta\gamma}. \quad (46)$$

In Eq. (46), α holds for x, y, z coordinates in the molecular frame and β, γ hold for 1, 2, 3 components of the vibration mode and for the Levi-Civita tensor there is the correspondence $(x, y, z) \rightarrow (1, 2, 3)$. ζ_3 is the Coriolis coupling constant and its expression is:

$$\zeta_3 = 1 - \frac{3}{2} \cos^2 \gamma. \quad (47)$$

γ has been already introduced in paper II. It can be partly derived from the experimental determination of ζ_3 . Finally, \mathbf{G}_3 is simply given by:

$$\mathbf{G}_3^\alpha = \zeta_3 \varepsilon_{\alpha\beta\gamma} q_{3\beta} p_{3\gamma}. \quad (48)$$

It satisfies the following commutation rules:

$$[\mathbf{G}_3^\alpha, \mathbf{G}_3^\beta] = i \zeta_3 \varepsilon_{\alpha\beta\gamma} \mathbf{G}_3^\gamma. \quad (49)$$

This leads to the definition of the vibrational angular momentum $\mathbf{I}_3 = \mathbf{G}_3 / \zeta_3$ which satisfies the normal commutation rules of a ‘true’ angular momentum. Now, we can re-consider the spin-vibration Hamiltonian of Eq. (38) when we restrict ourselves to the ν_3 mode. In that case, the only vibrational operators which give non-zero matrix elements are proportional to a component of \mathbf{I}_3 . The third term of Eq. (38) becomes:

$$H_{\text{SV}} = \sum_N \mathbf{I}_N \cdot {}^N \mathbf{V} \cdot \vec{\ell}_3, \quad (50)$$

where the components of a new spin-vibration tensor are defined by:

$${}^N \mathbf{V}_{\alpha\beta} = \varepsilon_{\beta\gamma\delta} \frac{1}{2} ({}^N \mathbf{V}_{3\gamma,3\delta} - {}^N \mathbf{V}_{3\delta,3\gamma})_\alpha, \quad (51)$$

$\alpha, \beta, \gamma, \delta$ designate the x, y, z coordinates of the ν_3 vibrational mode and are identified with the spatial molecular coordinates. This can be re-written as:

$${}^N \mathbf{V} = \zeta_3 {}^N \mathbf{C} + {}^N \mathbf{w} \quad (52)$$

where ${}^N \mathbf{C}$ is the spin-rotation tensor of Eq. (28) and ${}^N \mathbf{w}$ is a tensor deduced from the set of vectors of Eq. (37) and an equation similar to Eq. (51).

The symmetry of the ν_3 mode in OsO_4 is F_2 as it is the case for the ν_4 mode. Thus, the symmetry is not sufficient to define the vibrational mode. Let us introduce two particular vibrational modes of symmetry F_2 :

- $\nu^{(1)}$ for which the motions of the vibrating nuclei are parallel to each coordinate x, y, z of the molecular frame. Thus, the corresponding coefficients of the vibration are:

$$\left\{ \begin{array}{l} \vec{\ell}_{\text{Os},\alpha} = -\sqrt{\frac{4m_{\text{O}}}{M}} \vec{\alpha}, \end{array} \right. \quad (53a)$$

$$\left\{ \begin{array}{l} \vec{\ell}_{i,\alpha} = \sqrt{\frac{m_{\text{Os}}}{4M}} \vec{\alpha}, \end{array} \right. \quad (53b)$$

where $\alpha = x, y, z$ and $i = 1, 2, 3, 4$. These indices are associated to the four oxygen nuclei. The set of coefficients are associated to the three components $\nu_x^{(1)}, \nu_y^{(1)}, \nu_z^{(1)}$ of the mode $\nu^{(1)}$. They are related to the vibrational motion of the nuclei. As an example, $\nu_x^{(1)}$ is represented on Fig. 7. One can check easily that the corresponding Coriolis coupling constant is:

$$\zeta^{(1)} = 1. \quad (54)$$

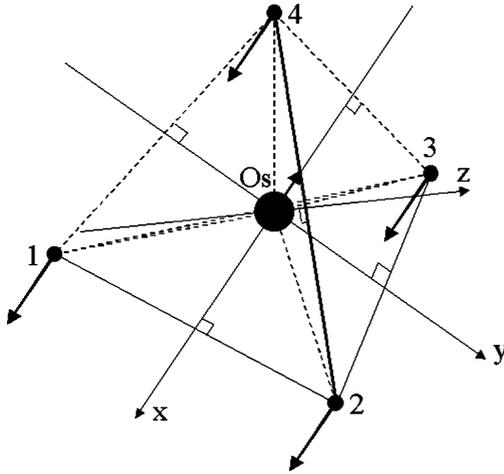


Fig. 7. Graphical representation of the x component, $v_x^{(1)}$, of one possible triply degenerate vibration mode of OsO_4 . The associated Coriolis coupling constant would be exactly 1.

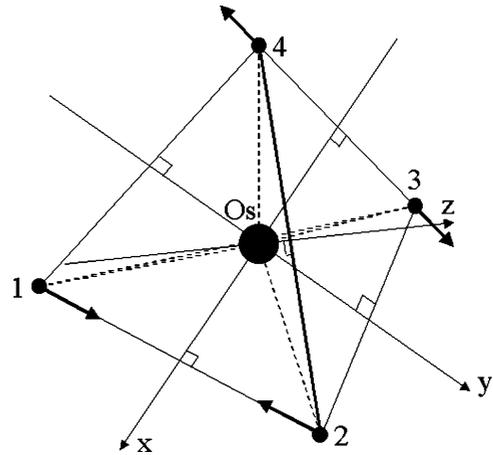


Fig. 8. Graphical representation of the x component, $v_x^{(-1/2)}$ of the triply degenerate vibration orthogonal to $v^{(1)}$. The associated Coriolis coupling constant would be $-1/2$. The true eigenmodes of OsO_4 are linear combinations of $v^{(1)}$ and $v^{(-1/2)}$.

– $v^{(-1/2)}$, orthogonal to the $v^{(1)}$ mode, for which the motions of the vibrating nuclei are perpendicular to each coordinate x , y , z of the molecular frame. The corresponding coefficients of the vibration are:

$$\left\{ \begin{array}{l} \vec{\ell}'_{\text{Os},\alpha} = 0, \end{array} \right. \quad (55a)$$

$$\left\{ \begin{array}{l} \vec{\ell}'_{1,x} = -\vec{\ell}'_{2,x} : \frac{1}{2\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}; \quad \vec{\ell}'_{3,x} = -\vec{\ell}'_{4,x} : \frac{1}{2\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}, \end{array} \right. \quad (55b)$$

$$\left\{ \begin{array}{l} \vec{\ell}'_{1,y} = -\vec{\ell}'_{4,y} : \frac{1}{2\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}; \quad \vec{\ell}'_{2,y} = -\vec{\ell}'_{3,y} : \frac{1}{2\sqrt{2}} \begin{pmatrix} -1 \\ 0 \\ -1 \end{pmatrix}, \end{array} \right. \quad (55c)$$

$$\left\{ \begin{array}{l} \vec{\ell}'_{1,z} = -\vec{\ell}'_{3,z} : \frac{1}{2\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}; \quad \vec{\ell}'_{2,z} = -\vec{\ell}'_{4,z} : \frac{1}{2\sqrt{2}} \begin{pmatrix} -1 \\ -1 \\ 0 \end{pmatrix}. \end{array} \right. \quad (55d)$$

These coefficients correspond to nuclei displacements along the edges of the tetrahedron. $v_x^{(-1/2)}$ is represented on Fig. 8. The Coriolis coupling constant associated to $v^{(-1/2)}$ is:

$$\zeta^{(-1/2)} = -\frac{1}{2} \quad (56)$$

The proper modes of the molecule are linear combinations of these two modes which can be formally defined as:

$$\left\{ \begin{array}{l} v_3 = \cos \gamma v^{(-1/2)} + \sin \gamma v^{(1)}, \end{array} \right. \quad (57a)$$

$$\left\{ \begin{array}{l} v_4 = -\sin \gamma v^{(-1/2)} + \cos \gamma v^{(1)} \end{array} \right. \quad (57b)$$

which is more precisely defined by the set of coefficients:

$$\left\{ \begin{array}{l} \vec{\ell}_{3,\text{Os},\alpha} = \cos \gamma \vec{\ell}'_{\text{Os},\alpha} + \sin \gamma \vec{\ell}_{\text{Os},\alpha}, \end{array} \right. \quad (58a)$$

$$\left\{ \begin{array}{l} \vec{\ell}_{3,i,\alpha} = \cos \gamma \vec{\ell}'_{i,\alpha} + \sin \gamma \vec{\ell}_{i,\alpha}, \end{array} \right. \quad (58b)$$

where $\alpha = x, y, z$ and $i = 1, 2, 3, 4$. Similar equations are introduced for the v_4 mode.

With these definitions, one retrieves the expression of Eq. (47) for ζ_3 while $\zeta_4 = 1/2 - \zeta_3$.

Now, we can give a complete expression of the spin-vibration tensor which reduces to a scalar, A , the spin-vibration constant, in the case of OsO_4 :

$${}^{\text{Os}}\mathbf{V}_{\alpha\alpha} = A = \zeta_3 c_a + c_a^n \left(\frac{1}{2} \cos^2 \gamma + \sqrt{\frac{M}{2m_{\text{Os}}}} \cos \gamma \sin \gamma \right) + \frac{4m_{\text{O}}}{M} \frac{\gamma_{\text{Os}} g_{\text{Os}} \mu_n}{Z_{\text{Os}} e} \left(\frac{\tilde{\omega}_3}{c} \right)^2 \sin^2 \gamma, \quad (59)$$

c_a^n is defined by Eq. (42a). We recognize three contributions:

- $\zeta_3 c_a$, that we will note A_{R} , comes from the spin-rotation interaction;
- the second one, proportional to Z_{O} , is the term due to the magnetic field created by the vibration of the oxygen nuclei. One can note that this term is sensitive to the relative sign of $\cos \gamma$ and $\sin \gamma$ which is not given by the knowledge of ζ_3 ;
- the last term has two physical origins. The first one is the motional magnetic field due to the electric field of the oxygen nuclei and induced by the vibration of the osmium nucleus. The corresponding contribution noted A_m is obtained from the third term of Eq. (59) by replacing γ_{Os} by 1. The second one is the Thomas precession with a contribution A_{T} which can be made explicit:

$$A_{\text{T}} = -\frac{m_{\text{O}}}{m_{\text{Os}}} \frac{2\hbar}{M} \left(\frac{\tilde{\omega}_3}{c} \right)^2 \sin^2 \gamma. \quad (60)$$

This contribution, proportional to the ratio between the outer nuclei and the central nucleus is, for example, 18 times larger for a molecule like $^{13}\text{CD}_4$ which absorbs also in the 10 μm region.

4.2.1. Numerical applications and discussion

We obtain a very rare situation for which the molecular constants involved in the expression of the spin-vibration constant are known. This is true except for the parameter γ . In fact, the value of ζ_3 obtained from the rovibrational analysis of the ν_3 band of OsO_4 and Eq. (47) leads to a set of two opposite values (modulo π) for γ :

$${}^{189}\text{OsO}_4 : \zeta_3 = 0.126927(14) \Rightarrow \gamma = \pm 0.702977(10) \text{ mod } \pi, \quad (61a)$$

$${}^{187}\text{OsO}_4 : \zeta_3 = 0.128169(19) \Rightarrow \gamma = \pm 0.703813(13) \text{ mod } \pi. \quad (61b)$$

The sign of $\cos \gamma \sin \gamma$ is undetermined. Thus, two values for the contribution A_n are possible: A_n^+ and A_n^- . We summarize in Table 3 the different contributions of the spin-vibration constant for the two isotopic species of OsO_4 considering the two possibilities and we compare the two possible final values A^+ and A^- with the experimental one.

Table 3
Various contributions to the spin-vibration constant and comparison with the experiment (in Hz)

${}^{189}\text{OsO}_4$	${}^{187}\text{OsO}_4$
$A_{\text{R}} = -2752.9(5)$	$A_{\text{R}} = -817.6(26)$
$A_n^+ = 236.40(4)$	$A_n^+ = 69.50(1)$
$A_n^- = -38.286(7)$	$A_n^- = -11.359(2)$
$A_m = 1.154(7)$	$A_m = 0.343(2)$
$A_{\text{T}} = -1.063(7)$	$A_{\text{T}} = -1.086(7)$
$A^+ = -2516.4(5)$	$A^+ = -748.8(26)$
$A^- = -2791.1(5)$	$A^- = -829.7(26)$
$A_{\text{exp}} = -2799(36)$	$A_{\text{exp}} = -781(27)$

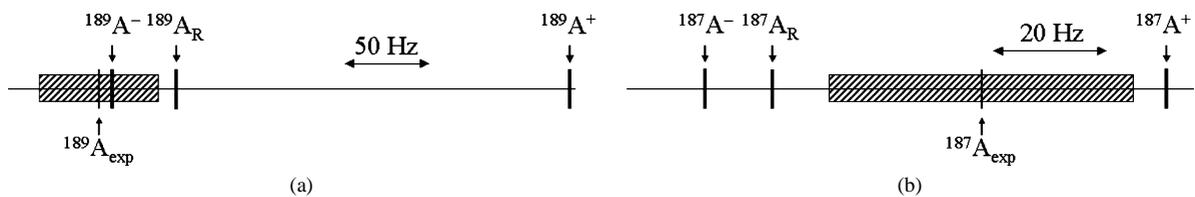


Fig. 9. Relative positions of the experimental spin-vibration constant, the constant $A_{\text{R}} = \zeta_3 c_a$ and the two possible theoretical choices A^+ and A^- : (a) case of ${}^{189}\text{OsO}_4$; (b) case of ${}^{187}\text{OsO}_4$.

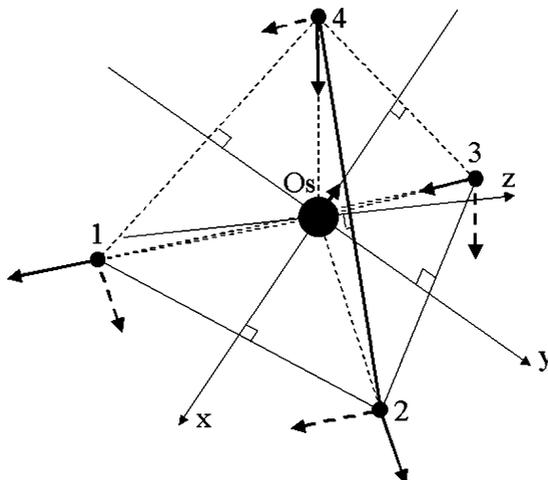


Fig. 10. x components of the two eigenmodes of OsO_4 of symmetry F_2 . The plain arrows correspond to ν_3 and the dotted arrows to ν_4 .

Fig. 9 displays this comparison. For both isotopic species, it is clear that the main contribution comes from A_R . In the case of $^{189}\text{OsO}_4$, the experimental accuracy permits to reveal the deviation from the approximate relation $A = \zeta_3 c_a$ and the observed value fits with the $-$ sign for the parameter γ , while the other choice is clearly rejected because the corresponding value is off by 8σ . For $^{187}\text{OsO}_4$, the observed value does not give the same agreement. A better agreement with the same sign for γ would be obtained with a 50 Hz-higher (absolute) value of $^{187}c_a$ which would shift in the same way the experimental value of ^{187}A . Such a shift is conceivable if one remembers that the determination of $^{187}c_a$ depends on the position of a weak crossover resonance affected by light shifts which could not be measured very satisfactorily.

The knowledge of the sign of γ determines unambiguously the vibrational mode, ν_3 and, thus, ν_4 . Fig. 10 shows the components ν_{3x} and ν_{4x} for these modes. It reveals that ν_{3x} essentially stretches the bonds Os–O while ν_{4x} bends the bonds O–Os–O. Thus, we expect a higher frequency for ν_3 than for ν_4 , close to ν_1 , which is the true stretching Os–O mode. This is exactly the situation since the frequencies of ν_1 , ν_3 and ν_4 are respectively 974 cm^{-1} , 975 cm^{-1} and 335 cm^{-1} . This analysis demonstrates that the magnetic hyperfine structure is indeed a very sensitive probe of the internal dynamics of molecules.

5. Conclusion

This paper completes the analysis of the hyperfine structure of the ν_3 band of $^{187}\text{OsO}_4$ and $^{189}\text{OsO}_4$. The resolution obtained by ultra-high resolution saturation spectroscopy has yielded an unprecedented experimental accuracy for magnetic hyperfine constants such as the spin-rotation and the spin-vibration constants. Our attempt to account for these phenomenological constants from first principles appears to be quite satisfactory. The same analysis remains to be done for two other molecules SF_6 and SiF_4 for which similar measurements of the magnetic hyperfine structure have been performed in our laboratory.

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