Chemical Physics 84 (1984) 159–165
North-Holland, Amsterdam

ADDENDUM TO SUPERFINE AND HYPERFINE STRUCTURES IN THE ν_3 BAND OF $^{32}SF_6$: EVIDENCE FOR A TENSOR SPIN–VIBRATION INTERACTION IN SPHERICAL TOPS [1)]

Jacques BORDÉ and Christian J. BORDÉ

*Laboratoire de Physique des Lasers, Associé au CNRS No 282, Université Paris-Nord,
Avenue J.B. Clément, 93430 Villetaneuse, France*

Received 29 July 1983

We give a first demonstration of a tensor spin–vibration interaction in the triply degenerate vibrationally excited state of a molecule. The corresponding coupling constant for $^{32}SF_6$ has been found to be equal to -6.75 kHz from a theoretical fit of the hyperfine structures of $P(4)F_1$ and of the $R(29)F_1^2F_2^1$ cluster in the ν_3 band around 10 µm. We also give a more accurate value of the tensor spin–rotation coupling constant, c_d, and the values of the reduced matrix elements of the relevant nuclear spin operators.

1. Introduction

The purpose of this short paper is to correct and extend somewhat the analysis of our previous paper [1] (referred to hereafter as I) on two specific points:

Firstly, a value of the tensor spin–vibration coupling constant is deduced from the values of the effective tensor spin–rotation constant in the excited vibrational state thanks to:
(i) an improved fit of the structure of $P(4)F_1$
(ii) the analysis of a well-resolved structure of the $R(29)F_2^1F_1^2$ cluster.

Secondly, we have corrected an erroneous reduced matrix element of a nuclear spin operator which results in a slight modification in the $R(28)A_2^0$ pattern; so we give a corrected figure 1 of I which also includes observed and calculated structures of $R(29)F_2^1F_1^2$. We seize this occasion to publish a computer-checked table of all the relevant nuclear spin reduced matrix elements.

2. Tensor spin–rotation and spin–vibration coupling constants

As pointed out in paper I the spin–vibration interaction can always be taken into account through an effective spin–rotation constant for each (J, R, l) manifold. This stems from the fact that the two interaction hamiltonians differ only through their rovibrational reduced matrix elements. In the case of the tensor interactions, eqs. (57) and (31) of paper I give the following factor between the matrix elements:

$$\lambda(J, R, l) = \frac{\langle J, Rl \| [D^{(1,1)} \times l_3^{(0,1)}]^{(1,2)} \| J, Rl \rangle}{\langle J, Rl \| [l^{(0,1)} \times D^{(1,1)}]^{(1,2)} \| J, Rl \rangle}. \quad (1)$$

---

[1] Work supported in part by DRET and by the Laboratoire de Spectroscopie Moléculaire, Université Pierre et Marie Curie, Paris, France.

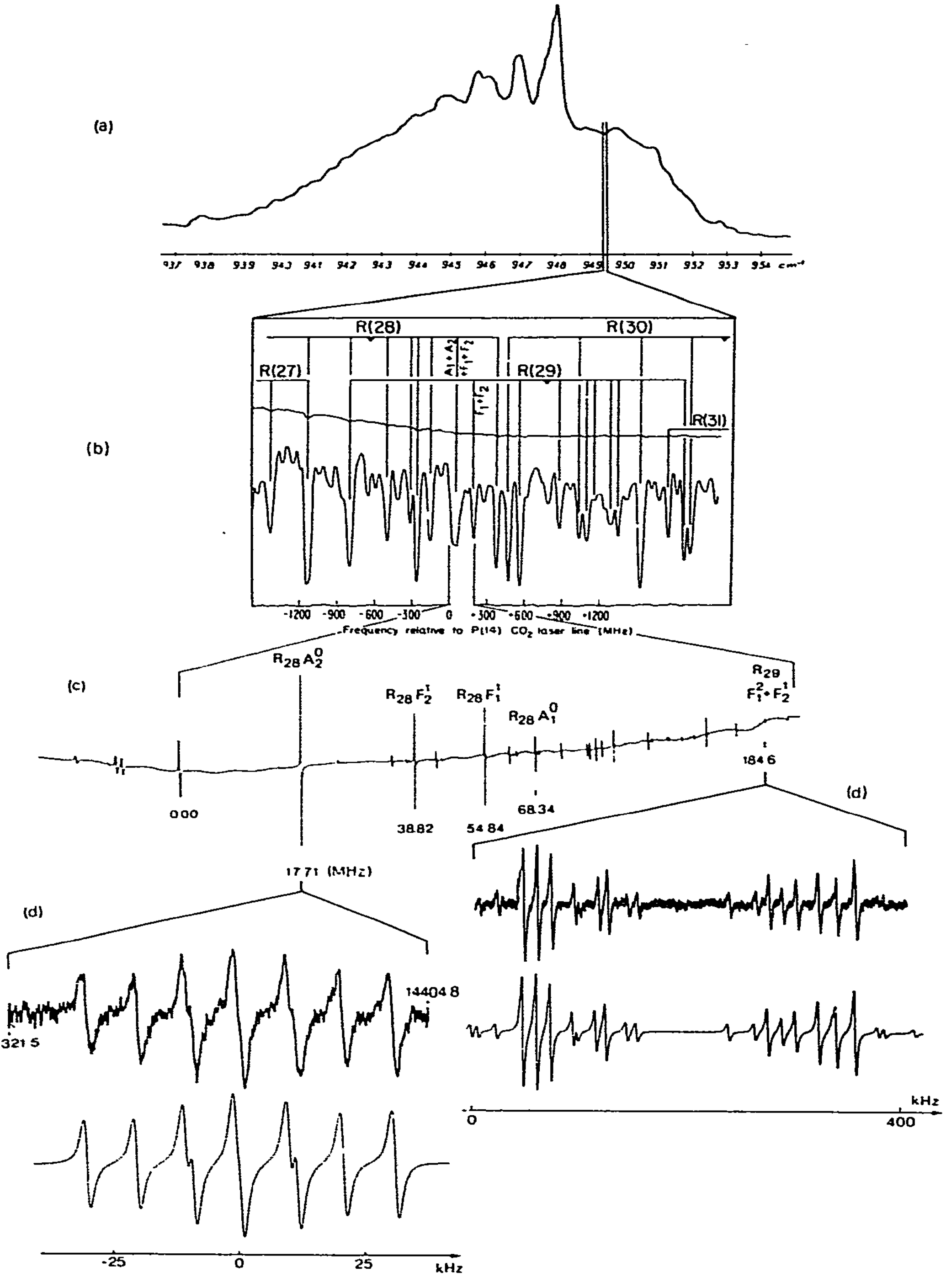

Fig. 1. Structure of the ν_3 band of $^{32}SF_6$ with increasing resolution: (a) envelope of the P, Q and R branches recorded with a conventional grating spectrometer; (b) Doppler-limited semiconductor diode laser spectrum exhibiting the tensor fine structure of *J*-manifolds: the superfine structure of clusters is resolved only in the saturation spectrum; (c) obtained with a free-running waveguide CO_2 laser, finally hyperfine structures are clearly resolved on saturation spectra; (d) obtained with a frequency-controlled spectrometer (phase-locked waveguide CO_2 laser [3]). For comparison calculated spectra are displayed below observed structures.

where

$$\langle J, Rl \| [D^{(1,1)} \times l_3^{(0,1)}]^{(1,2)} \| J, Rl \rangle$$

$$= (15/2)^{1/2}(2R+1)(2J+1)[l(l+1)(2l+1)]^{1/2} \begin{Bmatrix} 1 & J & J \\ 1 & l & l \\ 2 & R & R \end{Bmatrix} \qquad (2)$$

and where

$$\langle J, Rl \| [l^{(0,1)} \times D^{(1,1)}]^{(1,2)} \| J, Rl \rangle$$

$$= (-1)^{J+l+R}(15)^{1/2}(2R+1)(2J+1)[J(J+1)(2J+1)]^{1/2} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J \end{Bmatrix} \begin{Bmatrix} J & R & l \\ R & J & 2 \end{Bmatrix}. \qquad (3)$$

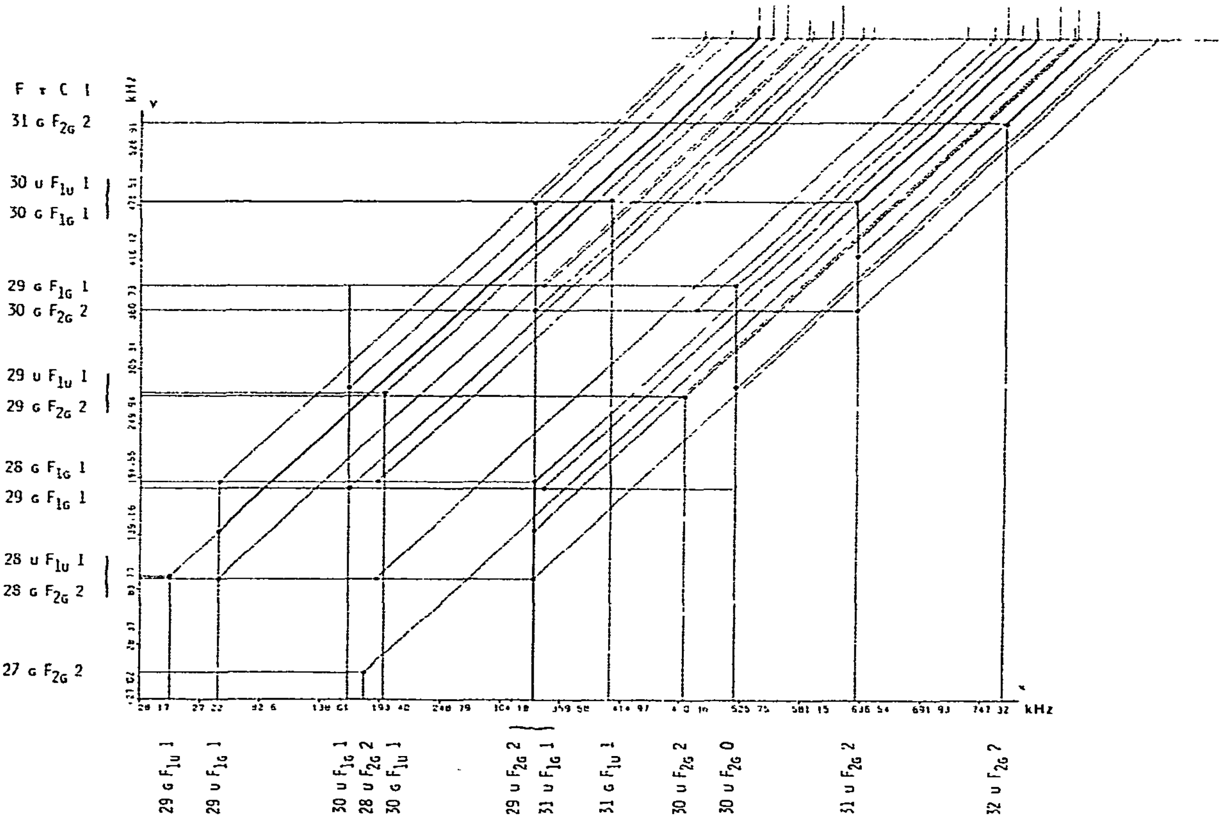

Fig. 2. Nomogram [7] for $R(29)F_1^2F_2^1$ which enables one to relate each feature in the spectrum to the pattern of levels. Eigenvalues are drawn along the y axis (x axis) for the lower (upper) vibrational state. Each allowed transition between two eigenvalues defines a point in the xy plane and the spectrum is obtained by a 45 degree projection of the set of points onto a horizontal line. In the case of crossovers involving two transitions the point to be projected is located halfway between the two points defined by the two transitions. The labels F, τ, C, I of the levels include the total angular momentum F, the parity τ, the O_h symmetry species C and the total nuclear spin I; however states with identical F and τ are strongly mixed and, for $F = J$ and $J \pm 1$, C and I lose completely their physical meaning; the labels C and I which are quoted in the figure are those associated with the largest components of the eigenvectors.

So, in the excited state and for given values of J, R and l, the effect of the spin–vibration interaction can be taken into account by replacing c_d with $c_d + \lambda(J, R, l)A_t$ where A_t denotes the tensor spin–vibration coupling constant (hA_t is equal to the constant X of eq. (57) of paper I). Thus, to determine A_t one can proceed as we did to obtain the scalar spin–vibration constant A [2]: measure effective tensor spin–rotation constants in the excited state in several (J, R, l) manifolds and try to relate them to a unique value of A_t. This approach will now be illustrated in the case of $R(29)F_1^2F_2^1$ and $P(4)F_1$.

(a) $R(29)F_1^2F_2^1$. A recent spectrum obtained with a phase-locked waveguide laser [3] is displayed in fig. 1. In addition to the 12 individual hyperfine components of the vibration–rotation lines, it shows crossover resonances with upper and lower common levels as illustrated by the nomogram of fig. 2. With the other constants fixed to their values given in paper I, the positions of these various components yield equations for the tensor spin–rotation constants in both states. The values obtained for c_d are $-4.60(\pm 0.05)$ and $-4.80(\pm 0.05)$ kHz for the lower and upper states respectively; in addition, in $v_3 = 1$, we have added -9 kHz to the energy of the F_2 vibration–rotation state calculated with t_{044} and t_{224}. This vibration–rotation correction is measured on the spectrum and is probably due to terms off-diagonal in R or to sixth-order terms. The value of -4.60 kHz for the ground state c_d is quite consistent with the uncertainty given for $|c_d|$ in ref. [4].

(b) $P(4)F_1$. As announced in a note added in proof to paper I, a large change in the value of c_d in the excited state gives an improved fit for $P(4)F_1$; this is shown in fig. 3 where $P(4)F_1$ is drawn with $c_d(v_3 = 0) = -4.60$ kHz (in agreement with $R(29)F_1^2F_2^1$) and $c_d(v_3 = 1) = -1.90$ kHz.

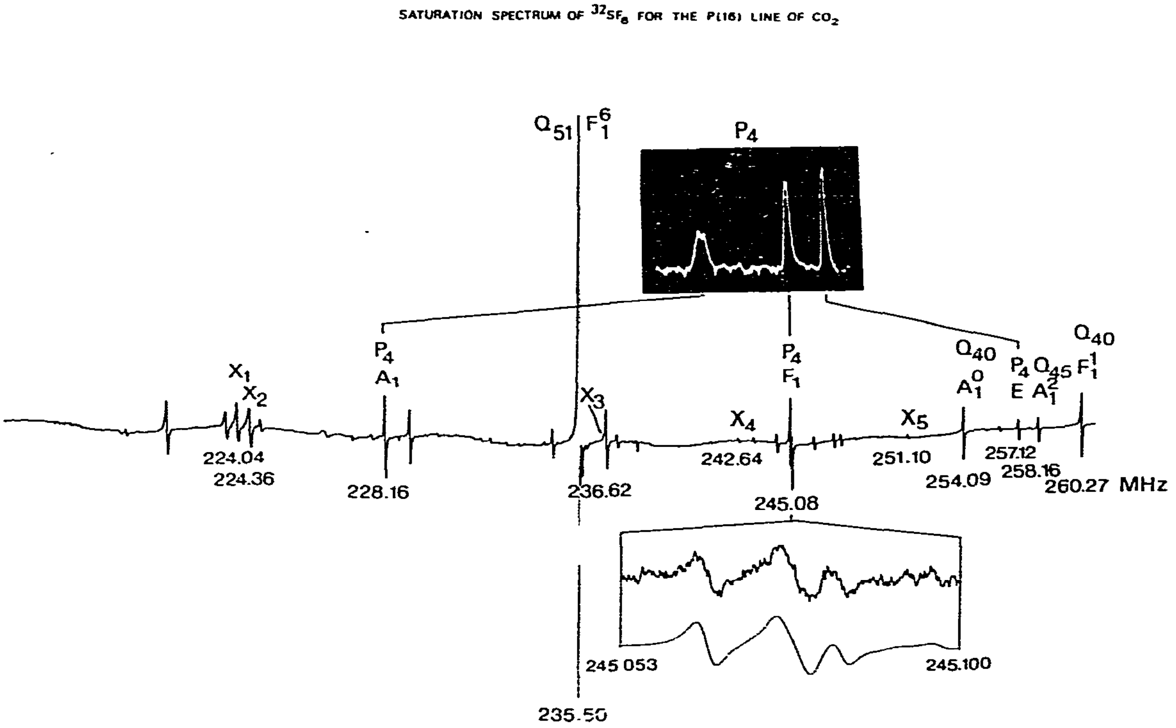

Fig. 3. Part of the P(4) manifold. Top: supersonic beam spectrum. Middle: saturation spectrum obtained with a free-running laser in a room-temperature cell (detunings are in MHz from Q(38)E°). Bottom: the $P(4)F_1$ component recorded with a frequency offset-locked waveguide laser is compared with the calculated spectrum.

The constant A_t which can be deduced from the P(4)F_1 case is equal to -6.75 kHz which in turn gives -4.83 kHz for $c_d(v_3=1)$ in R(29) in good agreement with the measured value. Any step further in accuracy requires the introduction of a true intrinsic dependence of the effective c_d on vibration (besides the effect of A_t); this affects the value of $c_d(v_3=1)$ by a quantity estimated to be less than 0.1 kHz which has a negligible influence in the cases of P(4)F_1 and R(29)$F_1^2F_2^1$.

3. Reduced matrix elements of nuclear spin operators

To calculate hyperfine structures, we need the numerical values of $\langle I, C_S|H_{NS}^{(J,C'')}||I', C_S'\rangle$ (see eq. (4) of I); these reduced matrix elements (RMEs) have been tabulated for various nuclear spin operators with the symmetry-adapted nuclear spin state vectors given in ref. [5]. The diagonal RMEs can be found in ref. [5] and the diagonal and off-diagonal RMEs of the elementary rank-one operators only are given in ref. [6]. The RMEs of rank-two operators can be calculated either directly from the Wigner–Eckart theorem or can be deduced (as we did) from the rank-one operator RMEs and the formula:

$$\langle I, C_S||[I^{(1,C)}\times I^{(1,C')}]^{(J,C'')}||I'C_S'\rangle = (-1)^{I+I'+J}(-1)^{C_S+C_S'+C''}[J]^{1/2}[C'']^{1/2}$$
$$\times\sum_{I_i,C_i}\begin{Bmatrix} J & 1 & 1\\ I_i & I & I'\end{Bmatrix}\begin{Bmatrix} C & C' & C''\\ C_S' & C_S & C_i\end{Bmatrix}\langle I, C_S||I^{(1,C)}||I_i, C_i\rangle\langle I_i, C_i||I^{(1,C')}||I', C_S'\rangle. \quad (4)$$

In order to make the comparison easier with some of the values already published in the above-mentioned literature, we give in table 1, the non-zero RMEs of

(i) the elementary operators $I^{(1,C)}$ (in agreement with ref. [6]).

(ii) the operators ${}_{C_1C_2}S^{(2,C)}$ with $C=\mathrm{E_g}$, $\mathrm{F_{2g}}$ which we used in paper I.

(iii) the operators ${}_{C_1C_1}S^{(0,A_{1g})}$ which may be needed in a near future.

The operators ${}_{C_1C_2}S^{(k,C)}$ are defined in eq. (44) of ref. [5] by

$${}_{C_1C_2}S^{(k,C)} = \tfrac{1}{2}\{[I^{(1,C_1)}\times I^{(1,C_2)}]^{(k,C)} + [I^{(1,C_2)}\times I^{(1,C_1)}]^{(k,C)}\} \quad (5)$$

and are related to the operators $[I\times I]^{(k,C)}$ which we introduced in I.

In particular for the operators with $k=2$ which we use, we have straightforwardly:

$$[I\times I]^{(2,C)}_{\mu,\sigma} = \sum_{\substack{i,j\\ i<j}}\sum_{C',\sigma'}\sum_{C'',\sigma''}\sum_{C''',\sigma'''}\langle C\sigma|ij\rangle\langle C'\sigma'|i\rangle\langle C''\sigma''|j\rangle$$
$$\times[C''']^{1/2}\alpha_{C'}\alpha_{C''}F^{C'C''C'''}_{\sigma'\sigma''\sigma'''}[I^{(1,C')}\times I^{(1,C'')}]^{(2,C''')}, \quad (6)$$

where the $\langle C\sigma|ij\rangle$ and $\langle C\sigma|i\rangle$ are the coefficients given in tables 2 [*] and 1 of I and $F^{C'C''C'''}_{\sigma'\sigma''\sigma'''}$ are the 3-C symbols of the $\mathrm{O_h}$ group. The α_C are the inverse of the factors appearing in eq. (25) of I between $I^{(1,C)}$ and $\Sigma_k\langle C\sigma|k\rangle I^{(1)k}$: $\alpha_{A_1}=6^{-1/2}$, $\alpha_E=-1/2$ and $\alpha_{F_1}=2^{-1/2}$ (Note that $6^{1/2}$ is actually missing in (25) and must be added). Finally, (6) leads to:

$$[I\times I]^{(2,\mathrm{E_g})} = -\tfrac{1}{6}\,{}_{\mathrm{A_{1g}E_g}}S^{(2,\mathrm{E_g})} + \tfrac{1}{16}\sqrt{2/3}\,{}_{\mathrm{E_gE_g}}S^{(2,\mathrm{E_g})} + \tfrac{1}{8}\sqrt{2}\,{}_{\mathrm{F_{1u}F_{1u}}}S^{(2,\mathrm{E_g})},$$
$$[I\times I]^{(2,\mathrm{E_g'})} = \tfrac{1}{16}\sqrt{6}\,{}_{\mathrm{E_gE_g}}S^{(2,\mathrm{E_g})} - \tfrac{1}{8}\sqrt{2}\,{}_{\mathrm{F_{1u}F_{1u}}}S^{(2,\mathrm{E_g})}, \quad (7)$$
$$[I\times I]^{(2,\mathrm{F_{2g}})} = \tfrac{1}{4}\sqrt{2}\,{}_{\mathrm{F_{1u}F_{1u}}}S^{(2,\mathrm{F_{2g}})}.$$

---

[*] In table 2 of I, one should read $-1/4$ instead of $-1/2$ for $\langle \mathrm{E_g'}2|26\rangle$.

Table 1

OP = $(J\ C_J \,\|\, OP \,\|\, J'\ C'_J)$	$I^{(1,A_{1g})}$	$I^{(1,E_g)}$	$I^{(1,F_{1u})}$	$_{A_{1g}E_g}S^{(2,F_g)}$	$_{E_gE_g}S^{(2,E_g)}$	$_{F_{1u}F_{1u}}S^{(2,E_g)}$	$_{F_{1u}F_{1u}}S^{(2,F_{2g})}$	$_{A_{1g}A_{1g}}S^{(0,A_{1g})}$	$_{E_gE_g}S^{(0,A_{1g})}$	$_{F_{1u}F_{1u}}S^{(0,A_{1g})}$
$(3\ A_{1g} \| OP \| 3\ A_{1g})$	$2\sqrt{21}$	0	0	0	0	0	0	$-4\sqrt{21}$	$-2\sqrt{14/3}$	$-\sqrt{7}$
$(3\ A_{1g} \| OP \| 2\ F_g)$	0	$2\sqrt{7}$	0	$4\sqrt{7}$	$-2\sqrt{14}/\sqrt{5}$	$-\sqrt{14}$	0	0	0	0
$(3\ A_{1g} \| OP \| 1\ E_g)$	0	0	0	0	$2\sqrt{21}$	$-\sqrt{7}$	0	0	0	0
$(3\ A_{1g} \| OP \| 2\ F_{1u})$	0	0	$-\sqrt{21}$	0	0	0	0	0	0	0
$(3\ A_{1g} \| OP \| 1\ F_{2g})$	0	0	0	0	0	0	$\sqrt{42}$	0	0	0
$(1\ A_{1g} \| OP \| 1\ A_{1g})$	$\sqrt{5}$	0	0	0	0	0	0	-2	$-16\sqrt{2/3}$	$-\sqrt{3}$
$(1\ A_{1g} \| OP \| 2\ E_g)$	0	$2\sqrt{3}$	0	$\sqrt{15}$	$-\sqrt{106}$	1	0	0	0	0
$(1\ A_{1g} \| OP \| 1\ E_g)$	0	$2\sqrt{5}$	0	$10/\sqrt{6}$	$-2/3$	$-\sqrt{3}$	0	0	0	0
$(1\ A_{1g} \| OP \| 2\ F_{1u})$	0	0	2	0	0	0	0	0	0	0
$(1\ A_{1g} \| OP \| 0\ F_{1u})$	0	0	$-\sqrt{5}$	0	0	0	0	0	0	0
$(1\ A_{1g} \| OP \| 1\ F_{2g})$	0	0	0	0	0	0	$-2\sqrt{7}$	0	0	0
$(0\ A_{2g} \| OP \| 0\ A_{2g})$	0	0	0	0	0	0	0	0	$-2\sqrt{6}$	-1
$(0\ A_{2g} \| OP \| 2\ E_g)$	0	0	0	0	$\sqrt{30}$	$-\sqrt{3}$	0	0	0	0
$(0\ A_{2g} \| OP \| 2\ E_g)$	0	$2\sqrt{3}$	0	0	0	0	0	0	0	0
$(0\ A_{2g} \| OP \| 1\ F_{2u})$	0	0	$\sqrt{3}$	0	0	0	0	0	0	0
$(0\ A_{2u} \| OP \| 0\ A_{2u})$	0	0	0	0	0	0	0	0	0	-3
$(0\ A_{2u} \| OP \| 2\ F_{1u})$	0	0	0	0	0	0	$\sqrt{6}$	0	0	0
$(0\ A_{2u} \| OP \| 1\ F_{2g})$	0	0	0	0	0	0	0	0	0	0
$(2\ E_g \| OP \| 2\ E_g)$	$\sqrt{60}$	$-\sqrt{10}$	0	$-\sqrt{15}$	$-\sqrt{70/3}$	$\sqrt{35/2}$	0	$-2\sqrt{30}$	$-8\sqrt{5/3}$	$-\sqrt{10}$
$(2\ E_g \| OP \| 1\ E_g)$	0	$\sqrt{30}$	0	$\sqrt{5}$*	$-\sqrt{30}$	$-\sqrt{10/2}$*	0	0	0	0
$(2\ E_g \| OP \| 2\ F_{1u})$	0	0	$\sqrt{15}$	0	0	0	0	0	0	0
$(2\ E_g \| OP \| 1\ F_{2g})$	0	0	0	0	0	0	$\sqrt{3}$	0	0	0
$(2\ E_g \| OP \| 1\ F_{2u})$	0	0	$-\sqrt{3}$	0	0	0	0	0	0	0
$(1\ E_g \| OP \| 1\ E_g)$	$\sqrt{12}$	$-\sqrt{5}$	0	$-\sqrt{21}$	$11\sqrt{13/3}$	$-\sqrt{15/2}$	0	$-2\sqrt{2}$	$-32/3$*	$-\sqrt{6}$
$(1\ F_g \| OP \| 2\ F_{1u})$	0	0	$-\sqrt{5}$	0	0	0	0	0	0	0
$(1\ E_g \| OP \| 0\ F_{1u})$	0	0	-2	0	0	0	0	0	0	0
$(1\ F_g \| OP \| 1\ F_{2g})$	0	0	0	0	0	0	$\sqrt{5}$	0	0	0
$(1\ E_g \| OP \| 1\ F_{2u})$	0	0	-3	0	0	0	0	0	0	0
$(2\ F_{1u} \| OP \| 2\ F_{1u})$	$\sqrt{60}$	$-\sqrt{30}$	0	$-\sqrt{105}$	$\sqrt{6}$	$\sqrt{35/6}$	$-\sqrt{35}$	$-6\sqrt{5}$	$-2\sqrt{10}$	$-5\sqrt{5/3}$
$(2\ F_{1u} \| OP \| 0\ F_{1u})$	0	0	0	0	$2\sqrt{3}$	$-\sqrt{10/3}$	$2\sqrt{5}$	0	0	0
$(2\ F_{1u} \| OP \| 1\ F_{2g})$	0	0	$-\sqrt{35}$	0	0	0	0	0	0	0
$(2\ F_{1u} \| OP \| 1\ F_{2u})$	0	$-\sqrt{30}$	0	$-3\sqrt{5}$	$-\sqrt{15}$	$3\sqrt{5/2}$	$3\sqrt{5}$	0	0	0
$(0\ F_{1u} \| OP \| 0\ F_{1u})$	0	0	0	0	0	0	0	0	$-4\sqrt{2}$	$-5/\sqrt{3}$
$(0\ F_{1u} \| OP \| 1\ F_{2g})$	0	0	$\sqrt{6}$	0	0	0	0	0	0	0
$(0\ F_{1u} \| OP \| 1\ F_{2u})$	0	$-2\sqrt{5}$	0	0	0	0	0	0	0	0
$(1\ F_{2g} \| OP \| 1\ F_{2g})$	$4\sqrt{2}$	$2\sqrt{6}$	0	$2\sqrt{5}$	$2\sqrt{10/3}$	$-\sqrt{10}$	$-2\sqrt{15}$	$-2\sqrt{3}$	$-4\sqrt{2/3}$	-7
$(1\ F_{2g} \| OP \| 1\ F_{2u})$	0	0	$3\sqrt{2}$	0	0	0	0	0	0	0
$(1\ F_{2u} \| OP \| 1\ F_{2u})$	$3\sqrt{2}$	$-\sqrt{6}$	0	$-\sqrt{5}$	$5\sqrt{10/3}$	$-\sqrt{5/2}$	$-\sqrt{15}$	$-2\sqrt{3}$	$-10\sqrt{2/3}$	-5*

One can easily check the relationships between d_F, d_1^E, d_2^E, d_3^E and d_1, d_2 given in (51) and (53) of I from (7) and from the expression of the hamiltonian (eq. (49) of I).

Except for four values which must be corrected in table 8 of ref. [5] and which we designate with an asterisk in our table 1, the two tables are in agreement. The transposed RMEs can be deduced through the formula

$$\langle I'C_S'\|H^{(J,C'')}\|IC_S\rangle = (-1)^{I'-I}(-1)^{C_S'+C_S+C''}\langle IC_S\|H^{(J,C'')}\|I'C_S'\rangle. \tag{8}$$

4. Conclusion

As a conclusion, we emphasize that, with this addendum, we have completed a first phase in the analysis of hyperfine spectra of SF_6 where the main interaction terms in the hamiltonian have been demonstrated from a limited number of structures. The next phase, which makes use of a large number of more precise structures measured with the phase-locked waveguide CO_2 laser [3], requires the introduction of higher-order terms in the hamiltonian and is presently being pursued.

References

[1] J. Bordé and Ch.J. Bordé, Chem. Phys. 71 (1982) 417.
[2] Ch.J. Bordé, M. Ouhayoun, A. van Lerberghe, Ch. Salomon, S. Avrillier, C.D. Cantrell and J. Bordé, in: Laser spectroscopy, Vol. 4, eds. H. Walther and K.W. Rothe (Springer, Berlin, 1979) p. 142.
[3] Ch. Salomon, Ch. Bréant, A. van Lerberghe, G. Camy and Ch.J. Bordé, Appl. Phys. B29 (1982) 153.
[4] J. Bordé, Ch.J. Bordé, Ch. Salomon, A. van Lerberghe, M. Ouhayoun and C.D. Cantrell, Phys. Rev. Letters 45 (1980) 14.
[5] F. Michelot, B. Bobin and J. Moret-Bailly, J. Mol. Spectry. 76 (1979) 374.
[6] F. Michelot, Thesis, University of Dijon, France (1980).
[7] W.G. Harter, C.W. Patterson and F.J. da Paixao, Rev. Mod. Phys. 50 (1978) 37.