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New Accurate Fit of an Extended Set of Saturation Data for the ν_3 Band of SF_6: Comparison of Hamiltonians in the Spherical and Cubic Tensor Formalisms

O. Acef,* Ch. J. Bordé,† A. Clairon,* G. Pierre,§ and B. Sartakov¶

*BNM-Laboratoire Primaire du Temps et des Fréquences, CNRS UMR 8630, Observatoire de Paris, 61 avenue de l'observatoire, 75014 Paris, France; †Laboratoire de Physique des Lasers, CNRS UMR 7538, Université Paris-Nord, Avenue J.-B. Clément, 93430 Villetaneuse, France; §Laboratoire de Physique de l'Université de Bourgogne, CNRS UMR 5027, Faculte des Sciences MIRANDE 9, Avenue Alain Savary BP 47870, 21078 Dijon Cedex, France; and ¶General Physics Institute, Russian Academy of Sciences, Vavilov Str. 38, 117942 Moscow, Russia

E-mail: Ouali.Acef@obspm.fr, chbo@ccr.jussieu.fr, pierre@jupiter.u-bourgogne.fr, lldgpi@redline.ru

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An extended set of 321 frequencies of vibration–rotation lines of the ν_3 band of SF_6 has been measured by saturation spectroscopy using various isotopic species of CO_2. A least-squares fit of these data has been performed using an effective Hamiltonian written either with a spherical tensor or with a cubic tensor formalism. We have derived correspondence formulas between the parameters in the two approaches and checked that both formalisms give the same results up to the seventh order. Corrected parameters are given for the fit with a fifth-order Hamiltonian. An accurate representation of the band is obtained at the tenth order (standard deviation $\approx$ 12 kHz) with a remarkable predictive power (better than 40 kHz) for J values ≤ 100. The convergence properties of the Hamiltonian power expansion are discussed. © 2000 Academic Press

Key Words: molecular spectroscopy; spherical top molecules; saturation spectroscopy.

1. INTRODUCTION: MOTIVATIONS AND EXPERIMENTAL DATA

In a first paper (hereafter referred to as Paper I) on this subject, published in 1987 (*1*), the goal was to obtain a global understanding and a theoretical fit of a full vibration–rotation band of a complex polyatomic molecule, obtained thanks to the modern techniques of optical frequency measurements and of sub-Doppler spectroscopy. What is meant by global understanding is, in fact, a test of an effective Hamiltonian, taking fully into account the symmetry properties of the molecule by group theoretical methods of tensor analysis. The ν_3 band of SF_6 appeared to us as a remarkable candidate for such a test because of the richness brought by the high symmetry of spherical tops and because of the experimental possibilities offered by saturation spectroscopy with CO_2 lasers, whose emission bands match this absorption band. Also, the ν_3 band of SF_6 seemed well-isolated, i.e., relatively free of perturbations from other vibration modes. This first attempt was only partly successful because there was a small unsuspected error in a fifth-order term of the Hamiltonian[1] and because the sample of measured frequencies was too limited. A number of lines had to be kept out of the fit and the residual standard deviation was significantly larger than the accuracy of the experimental data. In this paper, we make a new attempt toward the same goal, with a corrected Hamiltonian and with an extended set of experimental data. A second motivation for this work was to compare two ways to write the Hamiltonian, specifically using either a spherical tensor (as in I) or a cubic tensor formalism, and to show their equivalence and even to establish a correspondence table (Rosette stone) between them and their parameters.

The extended set of frequencies used in this paper has two origins. A first subset comprises the 136 vibration–rotation lines used and presented in detail in Paper I. These lines have been recorded (circa 1982) with the Villetaneuse saturation spectrometer (*2*, *3*) at the highest resolution at that time.[2] The hyperfine structure of these lines was fully resolved and a deconvolution procedure could be used to retrieve the true vibration–rotation frequencies with a few kilohertz accuracy. A second subset of 185 lines was recorded and measured at LPTF using other isotopic species of CO_2 (12, 13 for C; 16, 18 for O) in lasers illuminating external Fabry–Perot resonators filled with SF_6. In this case, the linewidth was limited by transit and power broadening to a larger value for which the hyperfine structure was not resolved. Furthermore, for tight superfine clusters, the hyperfine mixing of levels with different vibration–rotation symmetry species (*5*, *6*) gives rise to complicated asymmetrical structures which are only partly resolved. For a number of these cases we have calculated the expected struc-

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[1] In Paper I, the term $\sqrt{858}\ \eta\{264\} \times f(J, 5, 7)$ of Eq. [20] must be replaced by $\sqrt{858}\ \eta\{264\} \times f(J, 3, 5)$.

[2] Since then a new technique using slow molecules selection has been demonstrated and the linewidth has been reduced by another factor of 10 (*4*).

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ture to determine an approximate position of the true vibration–rotation line center (i.e., free of hyperfine effects). In many cases we could not use this calculated structure to perform an accurate deconvolution because these spectra were not recorded in low-laser field conditions giving rise to distortions through differential saturation of hyperfine components (and crossovers). For these lines this has resulted in a large uncertainty which we have usually fixed to the value of the frequency extension of the underlying unresolved structure (except in the case of exceptionally symmetric structures). All these frequencies have been used in the fits and are listed with their corresponding uncertainties in Table 1.

2. COMPARISON OF HAMILTONIANS IN THE SPHERICAL TENSOR AND CUBIC TENSOR FORMALISMS

2.1. Background

The vibration–rotation Hamiltonian of SF_6 in its ground electronic state can be expanded into a power series of the fundamental operators q_i, p_i, and J_α, where q_i and p_i are, respectively, the normal coordinates and the conjugate momenta of the vibrations and where J_α are the components of the angular momentum operator of the molecule in the molecular frame. The common case for semirigid molecules is a rapid decrease in the order of magnitude of the power expansion coefficients with increasing powers of the rotational and vibrational operators. This is related to the existence of an ordering parameter $\epsilon = (m/M)^{1/4}$ for the Born–Oppenheimer approximation (*8*), m being the mass of the electron and M being the mass of the molecule. The hierarchy of energies reads as $E_{\mathrm{rot}} \approx \epsilon^2 E_{\mathrm{vib}} \approx \epsilon^4 E_{\mathrm{el}}$, where E_{rot}, E_{vib}, and E_{el} are the rotational, vibrational, and electronic energies, respectively. This hierarchy breaks down at high values of quantum numbers. At the lowest order of approximation, the Hamiltonian is the sum of Hamiltonians for harmonic oscillators and for a rigid rotor. In the case where a vibrational mode of molecule is well isolated, i.e., if the vibrational levels under consideration are not in strong resonance with other vibrational states, the formalism of an effective Hamiltonian for the mode can be applied to calculate the corresponding vibration–rotation spectrum.

The effective Hamiltonian of the ν_3 mode of SF_6 is of spherical symmetry up to the first order of approximation when only the Coriolis interaction enters the zero-order Hamiltonian (*9*). The use of the $O(3)$ symmetry group makes it easier to classify the energy states and to derive the approximate selection rules for the transitions between the vibration–rotation states of the ν_3 mode. At a higher order of approximation, the symmetry of the vibration–rotation Hamiltonian of the ν_3 mode is reduced to O_h and it is convenient to classify the energy states and to calculate the vibration–rotation energy spectrum in the frame of a formalism using the symmetry point group.

In the case of the ν_3 mode all the fundamental operators (the vibrational momenta and coordinates as well as the angular momentum operators) and the vibrational and rotational wavefunctions can be classified in the frame of the $O(3)$ group. The tensor coupling scheme of the $O(3)$ group can be used to build up the complete sets of powers of operators and vibration–rotation wavefunctions. The subsequent procedure of reducing the spherical tensor spaces of a given rank to the irreducible representations of the point symmetry group must be used to get the basis sets classified by the symmetry with respect to the O_h group.

The alternative approach to the power expansion of the Hamiltonian is to start first with the classification of the fundamental operators and the vibrational and rotational wavefunctions in the frame of point group symmetry O_h and then to use the coupling procedure of the point symmetry group to build up the complete basis set of powers of operators and vibration–rotation wavefunctions.

Both approaches are equivalent in the case of the isolated ν_3 mode of XY_6 molecules of O_h symmetry and are used in this work for the calculation of the vibration–rotation spectra of the fundamental transitions of the ν_3 mode of SF_6. The advantage of the spherical tensor formalism is that it makes it easier to trace out the propensity rules which follow from the spherical symmetry of the first-order Hamiltonian while the advantage of the point symmetry group formalism is that it can be easily applied for the modeling of vibration–rotation spectra even in the cases where the ν_2 mode is involved and where the tensor formalism encounters the problem that ν_2 mode vibrational operators cannot be treated as spherical tensors.

The vibration–rotation Hamiltonian can be expanded into a power series of tensor operators $O^{\{i\}}$ in the frame of a given tensor formalism as

$$H = \sum_i c^{\{i\}} O^{\{i\}}, \qquad [1]$$

where $c^{\{i\}}$ are the power expansion coefficients, $\{i\}$ is an index which shows how the tensor operator was built from the fundamental operators. To facilitate the computer programming we use the annihilation and creation operators of the ν_3 vibrational mode as the fundamental operators instead of the momentum and coordinate operators. The well-known relations which define the creation a^+ and annihilation a operators versus the appropriate momentum p and coordinate q operators are

$$a = (q + ip)/\sqrt{2}; \quad a^+ = (q - ip)/\sqrt{2}. \qquad [2]$$

The commutation rules

$$[a, a] = 0; \quad [a, a^+] = 1; \quad [a^+, a^+] = 0 \qquad [3]$$

enable us to simplify the powers of operators composed of

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TABLE 1
Measured Vibration–Rotation Lines of the ν_3 Band of SF_6

ΔJ	J	C	n_0	n	n'	ν_{exp} (kHz)	$\Delta\nu^{(5)}$	$\Delta\nu$	σ	$\Delta\nu/\sigma$
P	94	$F1$	22	23	48	28201767543		5	30	0.17
P	94	$F2$	22	23	48	28201767543		5	30	0.17
P	88	$F1$	19	20	46	28223539522		−2	10	−0.21
P	88	$F2$	19	20	47	28223539522		−2	10	−0.21
P	94	$F2$	10	11	60	28223635961		−47	50	−0.95
P	94	$F1$	10	11	60	28223653367		−16	50	−0.33
P	87	$F1$	7	15	51	28236271728		13	300	0.05
P	87	$F2$	8	14	52	28236271728		11	200	0.06
P	90	$F1$	5	6	62	28236426577		2	20	0.12
P	88	$F2$	12	13	54	28236431548		1	50	0.03
P	88	$F1$	11	12	54	28236431905		20	50	0.40
P	90	E	3	4	42	28236433185		11	20	0.56
P	90	$F2$	5	6	62	28236439785		12	20	0.62
P	89	E	8	7	38	28236496876		−7	20	−0.36
P	84	$A1$	6	7	15	28236518520		0	20	0.05
P	84	E	11	12	31	28236518520		0	20	0.05
P	84	$F1$	17	18	45	28236518520		0	20	0.05
P	89	$F1$	13	10	58	28236521078		2	10	0.21
P	83	$F1$	13	8	55	28251749116	4	0	5	0.03
P	82	$F2$	10	11	51	28251854218	−56	2	5	0.44
P	82	$F1$	10	11	51	28251856339	−57	2	5	0.48
P	81	$F1$	8	13	49	28251999598	48	0	5	−0.03
P	81	$F2$	7	13	48	28251999615	48	0	5	−0.12
P	84	$A2$	1	2	20	28252005614	30	0	6	−0.12
P	84	$F2$	3	4	60	28252005891	30	0	5	−0.17
P	84	$F1$	3	4	59	28252006168	30	0	5	−0.11
P	84	$A1$	1	2	20	28252006444	30	0	5	−0.17
P	83	$F2$	14	7	56	28252056360	−30	0	3	−0.05
P	83	E	9	5	37	28252136051	−8	0	3	−0.15
P	75	E	7	5	33	28270087149		−5	10	−0.58
P	75	$F1$	11	8	49	28270127579		−4	10	−0.48
P	75	$A1$	3	3	16	28270261692		−2	20	−0.10
P	75	$F1$	12	7	50	28270438469		−3	20	−0.15
P	74	$F2$	10	11	45	28270438924		3	30	0.11
P	74	$F1$	9	10	46	28270440012		−9	30	−0.31
P	71	$F1$	7	11	43	28277099484		−3	30	−0.13
P	71	$F2$	8	10	44	28277100036		−5	30	−0.18
P	70	$F1$	11	12	41	28277114434		−3	20	−0.16
P	70	$F2$	12	13	40	28277114434		0	20	−0.04
P	74	E	0	1	37	28277116059		10	20	0.55
P	74	$F1$	0	1	55	28277116059		11	20	0.56
P	74	$F2$	0	1	55	28277116059		10	20	0.54
P	72	$F2$	6	7	48	28277199335		−2	10	−0.28
P	72	$F1$	6	7	47	28277278572		0	10	−0.02
P	72	$A1$	2	3	16	28277380603		6	10	0.65
P	67	$A2$	0	6	12	28277421453		0	5	0.10
P	67	E	0	11	23	28277421453		0	5	0.10
P	67	$F2$	1	16	35	28277421453		0	5	0.10
P	61	$F2$	12	3	43	28303347050		1	10	0.16
P	61	E	8	2	29	28303348300		0	10	0.08
P	61	$F1$	13	3	44	28303349531		0	10	0.06
P	60	$F2$	6	7	39	28303518992		−4	20	−0.20
P	60	$F1$	6	7	38	28303558771		3	20	0.16
P	58	$A2$	3	4	11	28303611145		0	20	−0.05
P	58	E	7	8	22	28303611145		0	20	−0.03

Note. J is the rotational quantum number of the lower state of the vibration-rotation transition; $\Delta J = J' - J$, where J' is the rotational quantum number of the upper state of the vibration-rotation transition; n_0 numbers the C symmetry sublevels within R multiplets in accordance with the definition given by Moret-Bailly [7], R being the approximate quantum number defined in the framework of the spherical tensor formalism via the coupling of vectors $\vec{J}$ and $\vec{l}$ as $\vec{R} = \vec{J} - \vec{l}$; n numbers the C symmetry sublevels of the ground vibrational state J multiplet in the frame of the cubic tensor formalism with increasing energy; n' numbers the C symmetry sublevels of the ν_3 vibrational state J' multiplet in the frame of the cubic tensor formalism with increasing energy; ν_{exp} is the measured value of the transition frequency; $\Delta\nu = \nu_{\mathrm{exp}} - \nu_{\mathrm{cal}}$ (kHz) where ν_{cal} is the calculated transition frequency with the tenth order Hamiltonian; $\Delta\nu^{(5)} = \nu_{\mathrm{exp}} - \nu_{\mathrm{cal}}^{(5)}$ (kHz) where $\nu_{\mathrm{cal}}^{(5)}$ is the calculated transition frequency with the fifth order Hamiltonian; σ is the experimental uncertainty of ν_{exp} (kHz).

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TABLE 1—*Continued*

ΔJ	J	C	n_0	n	n'	ν_{exp} (kHz)	$\Delta\nu^{(5)}$	$\Delta\nu$	σ	$\Delta\nu/\sigma$
P	58	$F2$	11	12	32	28303611145		0	20	−0.04
P	59	E	3	7	23	28303694697		−14	80	−0.19
P	59	$F1$	5	10	35	28303694783		−3	80	−0.05
P	59	$A1$	1	3	12	28303694933		−3	50	−0.07
P	57	$F1$	3	12	32	28305999064	−16	−3	5	−0.71
P	57	$F2$	3	11	32	28305999064	−16	−3	5	−0.79
P	58	$F2$	9	10	34	28306027542	−19	0	5	−0.18
P	58	$F1$	8	9	35	28306027756	−19	0	5	−0.19
P	59	$F1$	9	6	39	28306083696	8	−2	5	−0.49
P	60	$F1$	1	2	43	28306149748	−115	0	5	−0.12
P	60	E	0	1	30	28306149854	−115	−1	5	−0.23
P	60	$F2$	1	2	44	28306149961	−114	0	5	−0.10
P	59	$F2$	9	6	39	28306151890	8	1	5	0.21
P	59	$A2$	3	2	14	28306252637	20	0	1	0.27
P	55	$F1$	0	14	28	28306312965	28	−2	5	−0.45
P	55	$F2$	0	14	28	28306312965	28	−2	5	−0.45
P	56	$A2$	3	4	11	28306352767	−1	0	1	0.12
P	56	E	8	9	20	28306352767	−1	0	1	0.13
P	56	$F2$	12	13	30	28306352767	−1	0	1	0.13
P	59	$F2$	10	5	40	28306451162	−18	−1	5	−0.32
P	45	$F1$	0	12	23	28330140848		6	20	0.33
P	45	$F2$	0	11	23	28330140848		6	20	0.33
P	48	$F1$	2	3	33	28330255070		0	20	−0.01
P	48	E	1	2	23	28330263962		0	20	0.04
P	48	$F2$	2	3	34	28330272791		0	20	0.01
P	47	$F1$	4	8	28	28330301234		79	80	0.99
P	47	$F2$	5	7	29	28330302737		62	80	0.78
P	45	$F1$	8	4	31	28335916259		1	10	0.16
P	45	$F2$	7	4	30	28335960939		1	10	0.18
P	45	$A2$	2	2	10	28336000176		0	10	−0.09
P	33	$F1$	5	4	22	28359647866	−2	1	5	0.29
P	32	$F2$	7	8	17	28359656406	−41	0	5	−0.06
P	32	$F1$	6	7	17	28359656412	−40	0	5	0.09
P	33	$F2$	4	4	21	28359689209	0	1	5	0.25
P	33	$A2$	1	2	7	28359780516	0	0	1	−0.18
P	33	$F2$	5	3	22	28359881944	6	0	5	−0.02
P	33	E	3	2	15	28359915362	6	0	5	−0.11
P	33	$F1$	6	3	23	28359960590	8	0	5	−0.01
P	29	$F2$	5	2	20	28367811403		1	10	0.16
P	29	E	3	2	13	28367826853		1	10	0.20
P	29	$F1$	6	2	21	28367842257		2	10	0.28
P	28	$F1$	5	6	15	28367938185		−15	40	−0.39
P	28	$F2$	6	7	15	28367938185		16	40	0.42
P	21	$A2$	0	2	4	28382424957		−11	20	−0.58
P	21	$F2$	2	3	13	28382447556		0	20	0.00
P	21	E	1	2	9	28382461461		9	20	0.50
Q	89	E	13	2	17	28382554047		0	60	0.01
Q	89	$F1$	21	2	24	28382554047		1	60	0.03
Q	89	$F2$	20	2	24	28382554047		0	60	0.00
P	21	$F1$	3	3	14	28382578018		1	20	0.06
P	21	$F2$	3	2	14	28382659203		0	30	0.03
Q	85	E	7	7	21	28398914948		−32	40	−0.81
P	12	$F2$	1	2	8	28398918119		−12	20	−0.63
Q	80	$F2$	7	8	28	28398920573		−32	20	−1.62
Q	91	$F2$	11	12	35	28398926893		−35	20	−1.76
Q	91	$F1$	10	13	35	28398928442		−36	20	−1.85
Q	85	$F2$	11	10	31	28398931592		−33	20	−1.68
Q	77	$F1$	14	6	25	28398959221		−9	20	−0.48
Q	85	$A2$	3	4	11	28398963265		−35	20	−1.76
Q	70	$F2$	2	3	20	28398970433		4	20	0.22
Q	70	E	1	2	13	28398970925		2	20	0.13
Q	70	$F1$	2	3	21	28398971416		−1	20	−0.07
Q	79	$F2$	13	7	27	28398974025		−10	20	−0.51
P	12	$A2$	0	1	3	28398990799		5	15	0.37

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TABLE 1—*Continued*

ΔJ	J	C	n_0	n	n'	ν_{exp} (kHz)	$\Delta\nu^{(5)}$	$\Delta\nu$	σ	$\Delta\nu/\sigma$
Q	81	F2	12	8	28	28398995534		−1	30	−0.06
P	12	F2	0	1	9	28399016338		0	15	0.02
P	12	F1	0	1	8	28399030885		4	15	0.30
Q	77	A1	4	2	9	28399031627		0	20	0.04
P	12	A1	0	1	3	28399042129		9	15	0.61
Q	90	E	7	8	23	28399130200		58	50	1.18
Q	90	F1	11	12	35	28399131251		59	20	2.99
Q	90	A1	4	5	12	28399133345		60	30	2.03
Q	84	F1	9	10	31	28399182366		29	20	1.47
Q	67	A2	5	1	7	28399183966		0	10	0.00
Q	67	F2	15	2	19	28399184018		0	10	0.04
Q	67	F1	15	2	18	28399184067		−2	10	−0.23
Q	67	A1	4	1	7	28399184121		0	10	0.01
Q	78	A1	2	3	9	28399213992		15	20	0.80
Q	81	F1	12	9	29	28399220519		28	20	1.45
Q	84	F2	9	10	31	28399222726		32	20	1.64
Q	72	A1	1	2	7	28399288460		−4	20	−0.23
Q	72	F1	3	4	22	28399292078		−3	20	−0.19
Q	72	F2	3	4	22	28399295729		−7	20	−0.39
Q	64	E	0	1	11	28399299058		8	20	0.43
Q	64	F1	0	1	17	28399299058		5	20	0.29
Q	64	F2	0	1	17	28399299058		11	20	0.56
Q	72	A2	1	2	8	28399299425		−5	20	−0.27
Q	55	F2	6	8	22	28412340258	12	2	5	0.48
Q	55	F1	6	8	21	28412347656	25	4	5	0.99
Q	46	F1	3	4	16	28412376486	−41	−5	5	−1.12
Q	49	F1	7	6	18	28412382721	19	−1	5	−0.30
Q	47	F1	7	5	16	28412397039	65	1	5	0.30
Q	49	E	4	4	12	28412430671	40	0	5	0.05
Q	54	A2	2	3	7	28412442814	−21	0	5	−0.06
Q	54	F2	7	8	21	28412452980	−7	0	5	0.04
Q	54	E	4	5	14	28412457940	1	1	5	0.37
Q	41	F1	9	2	12	28412467435	−72	−3	5	−0.67
Q	41	E	5	2	9	28412472874	−73	−2	5	−0.55
Q	48	F1	4	5	17	28412474597	−35	−5	5	−1.06
Q	41	F2	8	2	12	28412478355	−76	−3	5	−0.63
Q	45	A2	2	2	5	28412526414	23	0	1	0.49
Q	53	F2	6	7	20	28412559609	−32	−1	5	−0.37
Q	53	F1	6	8	21	28412573094	−17	−1	5	−0.35
Q	38	F2	0	1	10	28412581959	−37	3	5	0.63
Q	38	E	0	1	7	28412582469	−35	5	5	1.08
Q	38	F1	0	1	11	28412582976	−39	2	5	0.40
Q	43	F1	8	3	13	28412599129	−41	0	5	−0.02
Q	45	F2	7	4	15	28412602224	5	0	5	−0.11
Q	48	F2	5	6	18	28412626007	49	2	5	0.44
Q	43	E	5	2	9	28412626400	−53	−4	5	−0.80
Q	43	F2	8	3	14	28412662331	−65	−1	5	−0.36
Q	47	E	4	4	12	28412662561	−8	1	5	0.26
Q	52	E	4	5	13	28412675428	−42	0	5	−0.02
Q	52	F1	6	7	20	28412684371	−35	−1	5	−0.40
Q	46	A1	1	2	6	28412685722	71	2	5	0.48
Q	45	F1	8	4	15	28412689322	−11	−1	5	−0.31
Q	52	A1	2	3	7	28412701510	−15	0	5	−0.03
Q	47	F2	7	5	17	28412736801	10	−1	5	−0.26
Q	51	F2	6	7	20	28412795369	−51	−2	5	−0.53
P	4	A1	0	1	1	28412810623	32	−1	5	−0.32
Q	51	F1	6	7	19	28412817981	−26	2	5	0.44
P	4	F1	0	1	2	28412827541	32	0	5	−0.18
Q	40	A1	0	1	4	28412836556	−44	0	5	0.05
P	4	E	0	1	2	28412839590	33	0	5	0.17
Q	45	A1	2	2	6	28412840627	−69	−4	5	−0.92
Q	40	F1	1	2	12	28412842743	−47	0	5	−0.07
P	3	F1	0	1	2	28414538220	26	3	50	0.07
Q	35	F1	7	2	10	28414544247	36	0	10	0.02

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TABLE 1—*Continued*

ΔJ	J	C	n_0	n	n'	ν_{exp} (kHz)	$\Delta\nu^{(5)}$	$\Delta\nu$	σ	$\Delta\nu/\sigma$
Q	43	$F1$	5	6	16	28414545046	−28	6	10	0.66
P	3	$F2$	0	1	2	28414556241	15	−6	20	−0.34
Q	35	E	4	2	8	28414557644	30	−3	10	−0.32
Q	39	$F2$	6	4	14	28414564734	39	0	10	0.02
Q	43	E	3	4	11	28414567138	−30	−3	10	−0.34
Q	35	$F2$	7	2	11	28414571252	28	−1	10	−0.18
P	3	$A2$	0	1	1	28414578726	8	−12	20	−0.62
Q	40	$A1$	1	2	5	28414592446	54	2	6	0.34
Q	37	$F1$	7	3	12	28414593720	44	2	6	0.44
R	5	$F1$	0	2	1	28429457684		0	20	0.01
R	5	$F2$	0	1	1	28429469331		1	20	0.09
R	5	E	0	1	1	28429499807		5	20	0.28
R	5	$F1$	1	1	2	28429505450		1	20	0.07
Q	69	$F1$	0	18	35	28429524124		0	10	0.06
Q	69	$F2$	0	17	34	28429524124		0	10	0.06
Q	91	$F1$	1	22	44	28429631478		0	18	−0.01
Q	91	$F2$	2	21	44	28429631478		0	18	−0.01
Q	80	$F1$	18	19	39	28429710807		−12	20	−0.65
Q	80	$F2$	19	20	40	28429710807		−12	20	−0.65
Q	82	$A2$	6	7	14	28433882126		1	10	0.14
Q	82	E	13	14	27	28433882126		1	10	0.14
Q	82	$F2$	20	21	41	28433882126		1	10	0.14
R	28	$F1$	2	3	5	28464417830	17	3	5	0.74
R	28	E	1	2	4	28464506923	4	1	5	0.34
R	28	$F2$	2	3	5	28464529560	2	1	5	0.24
R	28	$A2$	0	1	2	28464691303	−3	1	5	0.20
R	28	$F2$	1	2	6	28464712420	−4	3	5	0.61
R	28	$F1$	1	2	6	28464728434	−6	3	5	0.71
R	28	$A1$	0	1	3	28464741933	−11	0	1	−0.29
R	29	$F1$	2	6	3	28464858047	114	−3	5	−0.69
R	29	$F2$	1	6	2	28464858327	114	−2	5	−0.59
R	43	E	3	4	4	28484321195		−11	20	−0.60
R	43	$F1$	5	6	6	28484331355		−7	50	−0.16
R	47	$F1$	0	12	1	28484331404		47	50	0.96
R	47	$F2$	0	12	1	28484331404		47	50	0.96
R	43	$A1$	1	2	2	28484354807		0	20	0.05
R	42	$F1$	1	2	9	28484386921		1	20	0.05
R	42	E	0	1	7	28484389523		−1	20	−0.08
R	42	$F2$	1	2	10	28484392016		0	20	−0.01
R	43	$F1$	6	5	7	28484604034		−13	20	−0.65
R	45	$A2$	0	4	1	28484632411		13	50	0.27
R	45	E	1	6	2	28484632411		7	50	0.14
R	45	$F2$	2	9	3	28484632411		9	50	0.19
R	43	$F2$	6	5	7	28484650225		4	20	0.20
R	44	$F2$	7	8	4	28484675162		−4	30	−0.13
R	44	$F1$	6	7	5	28484675803		1	30	0.06
R	46	$A2$	1	2	3	28488295622		−2	15	−0.20
R	45	$F2$	9	2	10	28488431658		0	20	−0.03
R	45	E	6	1	7	28488433258		0	20	0.01
R	45	$F1$	10	2	11	28488434818		1	20	0.06
R	70	$F2$	7	8	11	28515795247	24	0	5	0.15
R	70	$F1$	7	8	10	28515836768	13	0	5	0.09
R	72	E	6	7	6	28515843955	36	0	5	0.02
R	72	$F2$	10	11	8	28515844150	36	0	5	0.01
R	72	$A2$	3	4	3	28515844541	36	0	5	0.08
R	74	E	8	9	5	28515857680	45	0	5	−0.05
R	74	$F2$	12	13	7	28515857682	45	0	5	−0.04
R	74	$A2$	3	4	3	28515857686	45	0	5	−0.02
R	89	$A1$	0	7	1	28515909384	56	1	16	0.11
R	89	E	0	15	1	28515909384	56	1	16	0.11
R	89	$F1$	1	22	2	28515909384	56	1	13	0.13
R	73	E	4	8	5	28515913350	35	0	5	−0.09
R	73	$F1$	7	12	8	28515913373	36	0	5	0.13
R	73	$A1$	2	4	3	28515913416	35	0	5	−0.04

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TABLE 1—*Continued*

ΔJ	J	C	n_0	n	n'	ν_{exp} (kHz)	$\Delta\nu^{(5)}$	$\Delta\nu$	σ	$\Delta\nu/\sigma$
R	66	$A2$	0	1	6	28516003631	6	0	1	−0.36
R	66	$F2$	0	1	17	28516003636	10	3	5	0.70
R	66	$F1$	0	1	16	28516003637	10	3	5	0.68
R	66	$A1$	0	1	6	28516003638	10	3	5	0.65
R	83	$A1$	0	6	1	28516052029	−35	−1	5	−0.24
R	83	E	1	13	2	28516052029	−35	−1	5	−0.24
R	83	$F1$	2	19	3	28516052029	−35	−1	5	−0.24
R	77	$F1$	5	15	6	28516080476	17	1	5	0.20
R	77	$F2$	4	15	5	28516080476	17	0	5	0.20
R	94	$A2$	7	8	1	28516092005	462	−2	30	−0.09
R	94	E	15	16	1	28516092005	462	−2	30	−0.09
R	94	$F2$	23	24	1	28516092005	462	−2	30	−0.09
R	70	$A1$	2	3	4	28516133528	0	0	5	0.04
R	86	$A1$	6	7	1	28516135490	−36	0	8	0.11
R	86	E	13	14	2	28516135490	−36	0	8	0.11
R	86	$F1$	19	20	2	28516135490	−36	0	8	0.11
R	69	$F2$	12	5	13	28516214198	−56	3	5	0.60
R	70	$F1$	6	7	11	28516224553	−21	0	5	−0.15
R	71	$F1$	9	9	10	28516235869	−12	−1	5	−0.30
R	69	E	8	3	9	28516236825	−60	0	5	−0.03
R	67	$A1$	4	1	5	28516240568	−49	0	5	−0.08
R	67	$F1$	15	2	16	28516240600	−49	0	5	−0.11
R	67	$F2$	15	2	16	28516240632	−49	0	5	−0.13
R	67	$A2$	5	1	6	28516240664	−49	0	5	−0.15
R	71	$F2$	9	9	10	28516246975	−17	−2	5	−0.40
R	69	$F1$	13	5	14	28516254852	−61	0	5	−0.10
R	81	$F1$	3	18	4	28516266540	−37	0	5	0.00
R	81	$F2$	3	17	4	28516266540	−37	0	5	0.00
R	84	$F1$	18	19	3	28516600484		0	20	0.04
R	84	$F2$	18	19	3	28516600484		0	20	0.04
R	87	$F1$	1	21	2	28516622164		1	20	0.09
R	87	$F2$	2	20	3	28516622164		1	20	0.09
R	75	$F1$	6	13	7	28516634279		5	20	0.26
R	75	$F2$	6	13	7	28516634279		2	20	0.13
R	73	$F1$	8	11	9	28516690153		−5	50	−0.11
R	73	$F2$	7	11	8	28516690447		9	50	0.20
R	70	$F1$	5	6	12	28516719501		4	20	0.23
R	71	$A2$	3	3	4	28516721259		−1	20	−0.09
R	74	$F1$	11	12	7	28516724677		−8	40	−0.21
R	74	$F2$	11	12	8	28516724677		21	40	0.55
R	91	$A2$	0	8	1	28516745934		1	20	0.09
R	91	E	0	15	1	28516745934		1	20	0.09
R	91	$F2$	1	22	2	28516745934		1	20	0.09
R	96	$A1$	8	9	1	28516750397		−6	60	−0.11
R	96	E	15	16	1	28516750397		−6	60	−0.11
R	96	$F1$	23	24	1	28516750397		−6	60	−0.11
R	71	$F2$	10	8	11	28516755438		5	20	0.27
R	78	$A1$	5	6	2	28516773679		0	20	−0.03
R	78	E	9	10	4	28516773679		0	20	−0.03
R	78	$F1$	14	15	5	28516773679		0	20	−0.03
R	71	E	6	6	7	28516774622		5	20	0.29
R	91	E	7	8	8	28534112756		4	100	0.05
R	91	$F1$	11	12	12	28534114193		6	30	0.22
R	91	$A1$	3	4	4	28534117089		7	100	0.08
R	90	E	6	7	9	28534117181		−5	100	−0.05
R	90	$F2$	10	11	13	28534124237		7	30	0.24
R	90	$A2$	3	4	5	28534138972		25	50	0.50
R	88	$F1$	7	8	15	28534163074		−7	30	−0.25
R	88	$A1$	2	3	6	28534255481		−13	16	−0.87
R	94	$F1$	13	14	10	28534306577		−43	60	−0.72
R	94	$F2$	13	14	11	28534306577		1	60	0.02
R	85	$F2$	17	4	18	28534319373		−3	30	−0.12
R	85	E	11	3	12	28534319651		−3	30	−0.11
R	85	$F1$	18	4	19	28534319930		−1	30	−0.06

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TABLE 1—*Continued*

ΔJ	J	C	n_0	n	n'	ν_{exp} (kHz)	$\Delta\nu^{(5)}$	$\Delta\nu$	σ	$\Delta\nu/\sigma$
R	84	E	1	2	13	28534337001		−17	60	−0.29
R	84	$F1$	2	3	19	28534337001		8	60	0.14
R	84	$F2$	2	3	19	28534337001		−42	60	−0.71
R	86	$F1$	4	5	17	28534370923		0	20	−0.02
R	86	E	3	4	12	28534373021		0	20	0.01
R	86	$F2$	4	5	18	28534375116		0	20	0.01
R	83	E	12	2	13	28534423049		5	30	0.20
R	83	$F1$	19	2	20	28534423049		4	30	0.15
R	83	$F2$	19	2	20	28534423049		7	30	0.25
R	89	$F1$	14	9	15	28534445866		19	20	0.99

annihilation and creation operators by putting all the creation operators to the left side from their noncommutating counterpart (normal ordering). The effective Hamiltonian of the vibrational states is diagonal in the principal vibrational quantum numbers. The use of creation/annihilation operators facilitates the selection from the powers of vibrational operators of only those which have equal powers of annihilation and creation operators and thus satisfy the above condition of a diagonal form for the effective Hamiltonian.

2.2. Symmetrized Operators in Both Groups

2.2.1. The Rotational Operators

In the spherical tensor formalism. The power operators $\mathcal{R}$ of the angular momentum operator J are built up and classified in the frame of the spherical tensor formalism as:

$$\mathcal{R}^{\Omega(K)} = \underbrace{(J \times J \times \cdots \times J)}_{\Omega}{}^{(K)} = (\mathbf{J}^2)^{(\Omega-K)/2} \cdot \underbrace{(((J \times J) \times \cdots) \times J)}_{K}{}^{(K)}. \qquad [4]$$

Here $\mathcal{R}$ is the spherical tensor rotational operator, Ω is the power of the angular momentum operator J; $\mathbf{J}^2 = J_X^2 + J_Y^2 + J_Z^2$; K is the rank of the spherical operator $\mathcal{R}$. The coupling of the spherical components of two spherical tensors is performed in accordance with the rules of the quantum theory of angular momenta:

$$T_{m_1}^{(K_1)} = \sum_{m_2, m_3} C_{K_2 m_2 K_3 m_3}^{K_1 m_1} \cdot T_{m_2}^{(K_2)} \cdot T_{m_3}^{(K_3)}, \qquad [5]$$

where $T_m^{(K)}$ is the m component of a spherical tensor of rank K and where $C_{K_2 m_2 K_3 m_3}^{K_1 m_1}$ is the Clebsch–Gordan coefficient.

In the cubic tensor formalism. The octahedral (cubic) formalism described here is deduced from the tetrahedral formalism (*10, 11*). In the octahedral formalism the components of the rotational operator $R^{\Omega(K,n\Gamma)}$ are the same as the spherical tensor $R^{\Omega(K)}$ (*7*) oriented in the O_h group,

$$R_\sigma^{\Omega(K,n\Gamma)} = R_{n\Gamma\sigma}^{\Omega(K)}, \qquad [6]$$

where Γ is the symmetry species relative to the O_h group, n distinguishes tensors with the same symmetry species in the O_h group, and σ is the component of the octahedral tensor.

These components introduced in (*7*) and called cubic components of spherical tensors can be given in terms of spherical components by

$$R^{\Omega(K)} = \underbrace{(R^{(1)} \times R^{(1)})^{(0)} \cdots (R^{(1)} \times R^{(1)})^{(0)}}_{(\Omega-K)/2} \times \underbrace{(((R^{(1)} \times R^{(1)}) \times \cdots) \times R^{(1)})^{(K)}}_{K} \qquad [7]$$

with elementary rotational operator $R_\sigma^{(1)} = 2J_\sigma$ and $(R^{(1)} \times R^{(1)})^{(0)} = (4/\sqrt{3})\mathbf{J}^2$

$$R_{n\Gamma\sigma}^{\Omega(K)} = \sum_m {}^{(K)}G_{n\Gamma\sigma}^{m} R_m^{\Omega(K)} \qquad [8]$$

where ${}^{(K)}G_{n\Gamma\sigma}^{m}$ are matrix elements of a unitary transformation (*12*).

The spherical components are given by the inverse transformation:

$$R_m^{\Omega(K)} = \sum_{n\Gamma\sigma} {}^{(K)}G_m^{n\Gamma\sigma} R_{n\Gamma\sigma}^{\Omega(K)}. \qquad [9]$$

2.2.2. The Vibrational Operators

In the spherical tensor formalism. In the case of the ν_3 mode, the creation and annihilation operators can be treated as tensors of rank 1_u of the group $O(3)$. The spherical components are defined from the Cartesian components by the following relations:

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$$\begin{array}{ll} a_{+1} = -(a_x + ia_y)/\sqrt{2} & a^{+}_{+1} = -(a^{+}_x + ia^{+}_y)/\sqrt{2} \\ a_0 = a_z & a^{+}_0 = a^{+}_z \\ a_{-1} = (a_x - ia_y)/\sqrt{2} & a^{+}_{-1} = (a^{+}_x - ia^{+}_y)/\sqrt{2}. \end{array} \quad [10]$$

In the case of the fundamental transition of the ν_3 mode the matrix elements of all the terms including annihilation or creation operators with a power higher than one are equal to zero. The zero power vibrational operator is 1. The operators relevant for the first vibrational state are defined by the tensor coupling relation

$$A^{(L_g)} = (a^{+(1_u)} \times a^{(1_u)})^{(L_g)}, \quad [11]$$

where the rank L of the resulting vibrational tensor can be 0, 1, or 2. Here the scalar coupling (scalar product) is defined as

$$(a^{+} \times a)^{(0)} = v, \quad [12]$$

where v is the principal vibrational quantum number of the ν_3 mode. The coupling to tensors of rank 1 and 2 uses the standard procedure for the spherical tensors yielding the following correspondence relations to the previously introduced (*13*) vibrational tensors

$$(a^{+} \times a)^{(1)} = -\mathbf{l}/\sqrt{2}; \quad (a^{+} \times a)^{(2)} = T^{(2)}, \quad [13]$$

where $\mathbf{l}$ is the vibrational angular momentum and $T^{(2)}$ is the rank 2 tensor vibrational operator of the ν_3 mode.

In the cubic tensor formalism. The elementary creation and annihilation operators (*14*) are expressed in terms of the dimensionless normal coordinates and momenta by

$$a_{s\sigma} = \frac{1}{\sqrt{2}}(q_{s\sigma} + ip_{s\sigma}) \quad [14]$$

$$a^{+}_{s\sigma} = \frac{1}{\sqrt{2}}(q_{s\sigma} - ip_{s\sigma}). \quad [15]$$

For the isolated ν_3 fundamental band ($s = 3$) the vibrational tensor operators are

$${}^{\epsilon}V_{3,3}^{F_{1_u}F_{1_u}(\Gamma)} = \frac{e^{i\phi}}{\sqrt{[\Gamma]}}(a_3^{+(F_{1_u})} \times a_3^{(F_{1_u})})^{(\Gamma)}, \quad [16]$$

where ϕ depends on the parity ϵ of the operator. Even operators ($\epsilon = +$) are obtained with $e^{i\phi} = 1$ and odd operators are obtained with $e^{i\phi} = -i$. $[\Gamma]$ is the dimension of the irreducible representation Γ.

2.2.3. *Rovibrational Operators*

In the spherical tensor formalism. The complete set of the powers of vibration–rotation operators of the Hamiltonian in the framework of the spherical formalism are built up as follows;

$$O^{\{\Omega,K,L,k,i\}} = (\mathscr{R}^{\Omega(K)} \times A^{(L)})^{(k)}_{A_{1_g},i}, \quad [17]$$

where k is the rank of the vibration–rotation operator in the framework of the $O(3)$. The index A_{1_g} shows that the reduction of the k rank tensor was done yielding the octahedral components of A_{1_g} symmetry; the running index i was used to number the different A_{1_g} representations which are contained in the spherical tensor space of rank k.

Finally the following form of Hamiltonian is used for computer calculations within the framework of the tensor formalism

$$H = H_0 + H_3, \quad [18]$$

where the ground state Hamiltonian is taken as

$$H_0 = \sum P_0^{\{\Omega,K,L=0,k=K,i\}} \cdot R^{\Omega(K)}_{A_{1_g},i} \quad [19]$$

and the ν_3 state vibration–rotation part of the Hamiltonian is taken as:

$$H_3 = \sum P_3^{\{\Omega,K,L,k,i\}} \cdot O^{\{\Omega,K,L,k,i\}}. \quad [20]$$

Here we use the subscript index 0 or 3, otherwise the indexing with $\{\Omega, K, L, k, i\}$ is not enough to distinguish between some ground state and the ν_3 state parameters P of the model Hamiltonian.

In the cubic tensor formalism. The complete set of the rovibrational operators T is built by coupling rotational and vibrational operators in the O_h group. In the case of the ground state the operators read as

$$T_0^{\Omega(K,n\Gamma)} = \beta R^{\Omega(K,n\Gamma=A_{1_g})}, \quad [21]$$

and in the case of $v_3 = 1$ state:

$$T_{3,3}^{\Omega(K,n\Gamma)} = \beta(R^{\Omega(K,n\Gamma)} \times {}^{\epsilon}V_{3,3}^{F_{1_u}F_{1_u}(\Gamma)})^{A_{1_g}}. \quad [22]$$

β is a numerical factor equal to $\sqrt{3}\,(-\sqrt{3}/4)^{\Omega/2}$ if $(K, n\Gamma) = (0, 0A_1)$, and equal to 1 otherwise.

The vibration–rotation Hamiltonian is described by formulae similar to the spherical tensor formalism

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TABLE 2
Correspondence between $O(3)$ and O_h Coupling Schemes

	Operators	
	O_h	$O(3)$
Rotational	$R^{\Omega(K,\Gamma)}$	$\mathscr{R}^{\Omega(K)}$
Vibrational	$A^{(\Gamma)} = \left(a_3^{+(1,F_{1u})'} \times a_3^{(1,F_{1u})}\right)^{(\Gamma)}$	$A^{(L)} = \left(a_3^{+(1)} \times a_3^{(1)}\right)^{(L)}$
Rovibrational	$\left(R^{\Omega(K,\Gamma)} \times A^{(\Gamma)}\right)^{(A_{1g})}$	$\left(\mathscr{R}^{\Omega(K)} \times A^{(L)}\right)^{(k)}_{A_{1g},i}$

	Basis Functions	
	O_h	$O(3)$
Rotational	$\Psi_r = \Psi^{(J,C_r,n_r)}$	$\Psi^{(J)}$
Vibrational	$\Psi_v = \Psi^{(\Gamma)}$	$\Psi^{(\ell)}$
Rovibrational	$(\Psi_r \times \Psi_v)^{(C)}$	$\Psi^{(R)}_{C,n} = \left(\Psi^{(J)} \times \Psi^{(\ell)}\right)^{(R)}_{C,n}$

$$H_0 = \sum t_0^{\Omega(K,n\Gamma=A_1)} \cdot T_0^{\Omega(K,n\Gamma=A_1)} \qquad [23]$$

$$H_3 = \sum t_{3,3}^{\Omega(K,n\Gamma)} \cdot T_{3,3}^{\Omega(K,n\Gamma)}, \qquad [24]$$

where $t_0^{\Omega(K,n\Gamma)}$ and $t_{3,3}^{\Omega(K,n\Gamma)}$ are the spectroscopic parameters.

2.2.4. *Symmetrized Basis Functions*

In the spherical tensor formalism. The basis set of vibration–rotation functions is constructed within this framework by using the formulae

$$\Psi^{(R)}_{C,n} = (\Psi^{(J)} \times \Psi^{(l)})^{(R)}_{C,n} \qquad [25]$$

where $\Psi^{(J)}$ is the rotational wavefunction for the angular momentum quantum number J, $\Psi^{(l)}$ is the vibrational wavefunction treated as a spherical tensor of rank l, where l is the vibrational angular momentum quantum number; the quantum number R is running from $|J - l|$ to $J + l$, the indices C and n are used to designate the octahedral components of the spherical tensor of rank R, C being the symmetry of the octahedral component and n the running index used to number the C symmetry components which belong to the tensor space of rank R. The ground state and fundamental state of the ν_3 mode are uniquely distinguished by the quantum number l which is equal to 0 in the ground state (vibrational symmetry $\Gamma = A_{1g}$) and to 1 in the $\nu_3 = 1$ state (vibrational symmetry $\Gamma = F_{1u}$).

In the cubic tensor formalism. In this framework the vibration–rotation functions are built with the same scheme as vibration–rotation operators. In the case of the ground state

$$\Psi^{(C)} = \Psi_r^{(J,n_rC_r=C)} \cdot \Psi_3^{(A_{1g})} \qquad [26]$$

and in the case of $\nu_3 = 1$ state:

$$\Psi^{(C)} = (\Psi_r^{(J,n_rC_r)} \times \Psi_3^{(F_{1u})})^{(C)}. \qquad [27]$$

The basis functions $\Psi^{(R)}_{C,n}$ of the *spherical construction* can be expressed as

$$\Psi^{(R)}_{C,n} = \sqrt{\frac{2R+1}{[C]}} \sum_{n_r,C_r} K^{(l\ J\ R)}_{(\Gamma\ n_rC_r\ nC)} (\Psi_r^{(J,n_rC_r)} \times \Psi_3^{(\Gamma)})^{(C)}, \qquad [28]$$

where the coefficient K is called an *isoscalar factor* of the chain of groups $O(3) \supset O_h$ and can be found for instance in (*15*).

A summary of the formulae for the basic sets of powers of operators and vibration–rotation wavefunctions is presented in Table 2 for spherical tensor coupling and for cubic symmetry group coupling.

2.2.5. *Matrix Elements*

In the spherical tensor formalism. The matrix elements of the power operators are calculated by using in this framework the Wigner–Eckart theorem and the F coefficients, first computed by Moret-Bailly (*7*),

$$\begin{aligned} &\langle J, v, l, R, C, n | O^{\{\Omega,K,L,k,i\}} | J', v', l', R', C', n' \rangle \\ &\quad = \prod_{RkR'} \cdot (-1)^R \cdot F^{R,k,R'}_{Cn,A_{1g}i,C'n'} \delta_{JJ'} \cdot \delta_{CC'} \\ &\qquad \times \langle J \| \mathfrak{R}^{\Omega(K)} \| J \rangle \cdot \langle vl \| A^{(L)} \| v'l' \rangle \cdot \begin{Bmatrix} L & K & k \\ l & J & R \\ l' & J & R' \end{Bmatrix}, \end{aligned} \qquad [29]$$

where $\Pi_{RkR'} = \sqrt{(2R+1) \cdot (2k+1) \cdot (2R'+1)}$, and $F^{R,k,R'}_{Cn,A_{1g}i,C'n'}$ is an F coefficient,

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$$\langle J \| \mathcal{R}^{\Omega(K)} \| J \rangle = [J(J+1)]^{(\Omega-K)/2} \times \left[\frac{K!}{(2K-1)!!} \frac{(2J+K+1)!}{(2J-K)!} \right]^{1/2} \Big/ 2^K, \quad [30]$$

and $\langle vl \| A^{(L)} \| v'l' \rangle$ are, respectively, the reduced matrix elements of the rotational and vibrational operators. The computer program, used in this work, is written in such a way that it gives the possibility of conducting the calculations of F coefficients, reduced matrix elements, and 9–j symbols for arbitrary values of quantum numbers and ranks L, K, and k of power operators. The only limitation is the specification of the computer that imposes an appropriate limitation to the dimensions of the matrices where the F coefficients are stored.

In the cubic tensor formalism. The matrix element of the vibration–rotation operator is diagonal in J and C quantum numbers and reads in the cubic formalism as:

$$\langle J, n_r, C_r; F_{1_u}; C, \sigma | T^{\Omega(K,n\Gamma)}_{3,3} | J, n'_r C'_r; F_{1_u}; C\sigma \rangle = -(-1)^{J+K} K^{(K\ J\ J)}_{(n\Gamma\ n'_r C'_r\ n_r C_r)} (-1)^{\Gamma+C+C'_r} \begin{pmatrix} F_{1_u} & C'_r & C \\ C_r & F_{1_u} & \Gamma \end{pmatrix} \times [\Gamma]^{-1/2} \langle J \| R^{\Omega(K)} \| J \rangle. \quad [31]$$

The reduced matrix elements of the rotational operator were first given in (*16*)

$$\langle J \| R^{\Omega(K)} \| J \rangle = [-4J(J+1)/\sqrt{3}]^{(\Omega-K)/2} \times \left[\frac{K!}{(2K-1)!!} \frac{(2J+K+1)!}{(2J-K)!} \right]^{1/2} \quad [32]$$

and $\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$ are 6C symbols which can be found for instance in (*15*).

2.3. Correspondence between the Two Formalisms

The formulae for the matrix elements of the basic powers of operators have been used to calculate the matrices of the basic operators for the vibration–rotation states with quantum numbers $v_3 = 0$, 1 and $J = 0, 1, 2, 3$. The computer program Mathematica has been used to expand a given cubic symmetry tensor matrix into the linear combination of the appropriate spherical tensor basic matrices. The expansion coefficients gave us the appropriate correspondence relations between the cubic tensor parameters and the spherical tensor parameters of the Hamiltonian. We have conducted the calculations for the operators up to the sixth order.

In Table 3 the calculated correspondence relations between tensor and symmetry point group parameters are given up to the sixth order in Ω. We also give in the same table the appropriate values of the cubic tensor parameters calculated from the values of the adjusted parameters of the tenth-order spherical tensor Hamiltonian (see Table 5).

FORTRAN programs have been written to convert the sixth-order set of spherical tensor parameters to the appropriate set of cubic tensor parameters and vice versa. A numerical test of these programs has been performed for some sets of parameters yielding a complete agreement between the simulated transition frequencies of the sixth-order model Hamiltonians.

3. THE FITTING PROCEDURE

The fitting of the frequencies of spectral lines was conducted using the second-order gradient technique and the Hamiltonian within the spherical tensor formalism. The mean-square deviation

$$S = \sum (\nu_{\text{obs}} - \nu_{\text{cal}})^2 / \sigma^2 \quad [33]$$

was taken as the sum of square deviations of the measured frequencies from the calculated ones over all measured lines. The deviations were also weighted by the experimental uncertainty σ of the measured frequency of the line. The calculated frequencies are functions of the set of parameters $\{P\}$ of the model vibration–rotation Hamiltonian. For a given set $\{P\}$ the mean-square deviation S was approximated to second order in the variations of the parameters $\{\delta P\}$

$$S = S_0 + \frac{\partial S}{\partial P_i} \cdot \delta P_i + \frac{1}{2} \cdot \frac{\partial^2 S}{\partial P_i \partial P_j} \cdot \delta P_i \cdot \delta P_j + \ldots . \quad [34]$$

The matrix $C_{i,j} = \partial^2 S / \partial P_i \partial P_j$ of second derivatives and the vector $F_i = -\partial S / \partial P_i$ have been calculated numerically and the iterative formulae

$$P_i := P_i + \sum_j (\hat{C}^{-1})_{i,j} \cdot F_j \quad [35]$$

have been applied to find the minimum of S. The eigenvalues of the matrix C have been analyzed to distinguish between saddle points and the real minima of S. The analysis of the eigenvalues of the C matrix at the minimum of S made it possible to reveal numerically the correlations between the parameters. Here we say that the parameters are correlated if we can express their variations via the variation along a direction x as

$$\delta P_i = a_i \delta x, \quad [36]$$

where a_i are the direction cosines, and if, along the direction x, the first derivative $\partial S / \partial x$ and the second derivative $\partial^2 S / \partial x^2$ are equal to zero. It means that by an appropriate small change of the parameters one can change the model Hamiltonian leaving the mean-square deviation unchanged. Some correla-

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TABLE 3

Correspondence between O_h and $O(3)$ Parameters up to Sixth Order

Order	H_{mn}	O_h	$O(3)$	Value (cm^{-1})
0	02	$t_0^{2(0,A_1)}$	$P_0^{2,0,0,0,1}$	$0.91077 \cdot 10^{-1}$
2	04	$t_0^{4(0,A_1)}$	$P_0^{4,0,0,0,1}$	$-0.65 \cdot 10^{-8}$
2	04	$t_0^{4(4,A_1)}$	$P_0^{4,4,0,4,1}/16$	$0.125 \cdot 10^{-9}$
4	06	$t_0^{6(0,A_1)}$	$P_0^{6,0,0,0,1}$	0*
4	06	$t_0^{6(4,A_1)}$	$-(\sqrt{3}/64)\ P_0^{6,4,0,4,1}$	0*
4	06	$t_0^{6(6,A_1)}$	$-P_0^{6,6,0,6,1}/256$	0*
6	08	$t_0^{8(0,A_1)}$	$P_0^{8,0,0,0,1}$	0*
6	08	$t_0^{8(4,A_1)}$	$(3/256)P_0^{8,4,0,4,1}$	0*
6	08	$t_0^{8(6,A_1)}$	$(\sqrt{3}/16)P_0^{8,6,0,6,1}$	0*
6	08	$t_0^{8(8,A_1)}$	$P_0^{8,8,0,8,1}/256$	0*
0	20	$t_{3,3}^{0(0,A_1)}$	$P_3^{0,0,0,0,1}$	948.10250821
1	21	$t_{3,3}^{1(1,F_1)}$	$(\sqrt{3}/2)\ P_3^{1,1,1,0,1}$	0.267556922
2	22	$t_{3,3}^{2(0,A_1)}$	$P_3^{2,0,0,0,1}$	$-0.13105415 \cdot 10^{-3}$
2	22	$t_{3,3}^{2(2,E)}$	$-(\sqrt{5}/10)P_3^{2,2,2,0,1} - \sqrt{3/40}P_3^{2,2,2,4,1}$	$-0.15849730 \cdot 10^{-3}$
2	22	$t_{3,3}^{2(2,F_2)}$	$-(3\sqrt{5}/20)P_3^{2,2,2,0,1} + \sqrt{3/40}P_3^{2,2,2,4,1}$	$0.4383740 \cdot 10^{-4}$
3	23	$t_{3,3}^{3(1,F_1)}$	$-(3/8)P_3^{3,1,1,0,1}$	$0.3325527 \cdot 10^{-7}$
3	23	$t_{3,3}^{3(3,F_1)}$	$-(\sqrt{3}/8)P_3^{3,3,1,4,1}$	$-0.11391 \cdot 10^{-8}$
4	24	$t_{3,3}^{4(0,A_1)}$	$P_3^{4,0,0,0,1}$	$-0.47350 \cdot 10^{-10}$
4	24	$t_{3,3}^{4(2,E)}$	$(\sqrt{15}/40)P_3^{4,2,2,0,1} + (3\sqrt{40}/160)P_3^{4,2,2,4,1}$	$0.16070 \cdot 10^{-10}$
4	24	$t_{3,3}^{4(2,F_2)}$	$(3\sqrt{15}/80)P_3^{4,2,2,0,1} - (3\sqrt{40}/160)P_3^{4,2,2,4,1}$	$0.12493 \cdot 10^{-10}$
4	24	$t_{3,3}^{4(4,A_1)}$	$(\sqrt{3}/16)P_3^{4,4,0,4,1}$	$-0.11350 \cdot 10^{-10}$
4	24	$t_{3,3}^{4(4,E)}$	$-(1/4\sqrt{11})P_3^{4,4,2,4,1} + (\sqrt{3}/8\sqrt{22})P_3^{4,4,2,6,1}$	$0.29983 \cdot 10^{-11}$
4	24	$t_{3,3}^{4(4,F_2)}$	$-(3/16\sqrt{11})P_3^{4,4,2,4,1} - (\sqrt{3}/4\sqrt{22})P_3^{4,4,2,6,1}$	$-0.5996 \cdot 10^{-11}$
5	25	$t_{3,3}^{5(1,F_1)}$	$(3\sqrt{3}/32)P_3^{5,1,1,0,1}$	$-0.15333 \cdot 10^{-12}$
5	25	$t_{3,3}^{5(3,F_1)}$	$(3/32)P_3^{5,3,1,4,1}$	$0.9888 \cdot 10^{-13}$
5	25	$t_{3,3}^{5(5,0F_1)}$	$\sqrt{\frac{3}{11}}\,\frac{(\sqrt{21}+5)}{64\sqrt{6+\sqrt{21}}}\,P_3^{5,5,1,4,1} + \frac{\sqrt{3}\,(7-\sqrt{189})}{64\sqrt{77}\,\sqrt{6+\sqrt{21}}}\,P_3^{5,5,1,6,1}$	$0.47182 \cdot 10^{-14}$
5	25	$t_{3,3}^{5(5,1F_1)}$	$-\sqrt{\frac{3}{11}}\,\frac{(\sqrt{21}-5)}{64\sqrt{6-\sqrt{21}}}\,P_3^{5,5,1,4,1} + \frac{\sqrt{3}\,(7+\sqrt{189})}{64\sqrt{77}\,\sqrt{6-\sqrt{21}}}\,P_3^{5,5,1,6,1}$	$-0.3964 \cdot 10^{-13}$
6	26	$t_{3,3}^{6(0,A_1)}$	$P_3^{6,0,0,0,1}$	$-0.48169 \cdot 10^{-15}$
6	26	$t_{3,3}^{6(2,E)}$	$-\frac{3\sqrt{5}}{160}P_3^{6,2,2,0,1} - \frac{3\sqrt{30}}{320}P_3^{6,2,2,4,1}$	$-0.22172 \cdot 10^{-15}$
6	26	$t_{3,3}^{6(2,F_2)}$	$-\frac{9\sqrt{5}}{320}P_3^{6,2,2,0,1} + \frac{3\sqrt{30}}{320}P_3^{6,2,2,4,1}$	$-0.38284 \cdot 10^{-15}$
6	26	$t_{3,3}^{6(4,A_1)}$	$-\frac{3}{64}P_3^{6,4,0,4,1}$	$0.1579 \cdot 10^{-15}$
6	26	$t_{3,3}^{6(4,E)}$	$\frac{\sqrt{3}}{16\sqrt{11}}P_3^{6,4,2,4,1} - \frac{3}{32\sqrt{22}}P_3^{6,4,2,6,1}$	$0.26453 \cdot 10^{-16}$
6	26	$t_{3,3}^{6(4,F_2)}$	$\frac{3\sqrt{3}}{64\sqrt{11}}P_3^{6,4,2,4,1} + \frac{3}{16\sqrt{22}}P_3^{6,4,2,6,1}$	$-0.5290 \cdot 10^{-16}$
6	26	$t_{3,3}^{6(6,A_1)}$	$-\sqrt{3}/64P_3^{6,6,0,6,1}$	$-0.37532 \cdot 10^{-16}$
6	26	$t_{3,3}^{6(6,E)}$	$-\frac{\sqrt{30}}{64\sqrt{143}}\,P_3^{6,6,2,4,1} + \frac{\sqrt{110}}{1760}\,P_3^{6,6,2,6,1}$ $-\frac{\sqrt{4290}}{4166}\,P_3^{6,6,2,8,1}$	$0.4090 \cdot 10^{-16}$
6	26	$t_{3,3}^{6(6,0F_2)}$	$\frac{3\sqrt{30}\,(23-\sqrt{421})}{128\sqrt{26}\,\sqrt{1684-79\sqrt{421}}}\,P_3^{6,6,2,4,1}$ $+\frac{3\,(\sqrt{421}-1)}{128\sqrt{5}\,\sqrt{1684-79\sqrt{421}}}\,P_3^{6,6,2,6,1}$ $-\frac{\sqrt{195}\,(79-4\sqrt{421})}{2080\,\sqrt{1684-79\sqrt{421}}}\,P_3^{6,6,2,8,1}$	$-0.675 \cdot 10^{-17}$
6	26	$t_{3,3}^{6(6,1F_2)}$	$-\frac{3\sqrt{30}\,(23+\sqrt{421})}{128\sqrt{26}\,\sqrt{1684+79\sqrt{421}}}\,P_3^{6,6,2,4,1}$ $+\frac{3\,(1+\sqrt{421})}{128\sqrt{5}\,\sqrt{1684+79\sqrt{421}}}\,P_3^{6,6,2,6,1}$ $+\frac{\sqrt{195}\,(79+4\sqrt{421})}{2080\,\sqrt{1684+79\sqrt{421}}}\,P_3^{6,6,2,8,1}$	$-0.488 \cdot 10^{-16}$

Note. The parameters marked by an asterisk have been fixed to zero.

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TABLE 4

Correspondence between the Adjusted Parameters of the Fifth-Order Hamiltonian and the Parameters Used in Paper I

$P_{n=0,3}^{\Omega,K,L,k,i}$	Parameter	Value in cm^{-1}
$P_0^{2,0,0,0,1}$	B_0	$9.1077(13) \cdot 10^{-2}$
$P_0^{4,0,0,0,1}$	γ_o	$-6.5(25) \cdot 10^{-9}$
$P_0^{4,4,0,4,1}/(4\sqrt{70})$	ε_o	$6.3(30) \cdot 10^{-11}$
$P_0^{6,0,0,0,1}$	π_0	$\pm 2 \cdot 10^{-13}$
$P_0^{6,4,0,4,1}/\sqrt{1120}$	ρ_0	$1.2(6) \cdot 10^{-14}$
$P_0^{6,6,0,6,1}/(64\sqrt{66})$	ξ_0	$7.1(2) \cdot 10^{-18}$
$P_3^{0,0,0,0,1}$	ν_{01}	$948.10251(3)$
$P_3^{1,1,1,0,1}/\sqrt{24}$	$(B_0\zeta)$	$6.3064(12) \cdot 10^{-2}$
$P_3^{2,0,0,0,1}$	$B_3 - B_0 = Y_3$	$-1.3105(2) \cdot 10^{-4}$
$-P_3^{2,2,2,0,1}/(12\sqrt{5})$	δ	$-7.6437(7) \cdot 10^{-6}$
$-P_3^{2,2,2,4,1}/\sqrt{280}$	φ	$-2.45795(3) \cdot 10^{-5}$
$-P_3^{3,1,1,0,1}/\sqrt{24}$	χ	$1.8(4) \cdot 10^{-8}$
$-P_3^{3,3,1,4,1}/(8\sqrt{35})$	μ	$-7.9(115) \cdot 10^{-10}$
$-P_3^{4,0,0,0,1}$	$\Delta\gamma$	$-4.5(3) \cdot 10^{-11}$
$-P_3^{4,2,2,0,1}/(12\sqrt{5})$	ψ	$-5.22(24) \cdot 10^{-12}$
$-P_3^{4,2,2,4,1}/\sqrt{280}$	σ	$2.01(3) \cdot 10^{-12}$
$P_3^{4,4,0,4,1}/(4\sqrt{70})$	$\Delta\varepsilon$	$-2.96(2) \cdot 10^{-14}$
$P_3^{4,4,2,4,1}/\sqrt{120}$	$T_{244} \sim \tau$	$0*$
$-P_3^{4,4,2,6,1}/(8\sqrt{231})$	η	$-6.13(2) \cdot 10^{-13}$
$-P_3^{5,1,1,0,1}/\sqrt{24}$	a_5	$2.7(60) \cdot 10^{-13}$
$P_3^{5,3,1,4,1}/\sqrt{2240}$	b_5	$-4.4(2) \cdot 10^{-14}$
$-\sqrt{5/11088}\, P_3^{5,5,1,4,1}$	c_5	$0*$
$P_3^{5,5,1,6,1}/\sqrt{7392}$	d_5	$1.01(1) \cdot 10^{-14}$
$P_3^{6,0,0,0,1}$	$\Delta\pi$	$-1.51(4) \cdot 10^{-15}$
$-P_3^{6,4,0,4,1}/\sqrt{120}$	$\Delta\rho$	$-4.7(1) \cdot 10^{-16}$
$P_3^{6,6,0,6,1}/(16\sqrt{231})$	$\Delta\xi$	$1.69(2) \cdot 10^{-17}$

Note. The third column gives the corrected values. (Only the 136 lines used in I were included the fit.) The parameters marked by an asterisk were fixed to zero.

tions arise owing to the contact transformation invariance (*17*). These correlations were confirmed numerically in the course of the fittings. To break the correlations, some parameters of the model Hamiltonian were strictly fixed to zero according to Table 3 of Ref. (*18*).

3.1. Fifth-Order Fit: Correlations between Parameters and Convergence of the Power Expansion

The above fitting procedure was applied to fit the set of lines observed in (*1*) with the fifth-order expansion of the Hamiltonian. The corrected parameters of the fifth-order Hamiltonian are given in Table 4. This fit yielded a standard deviation of about 80 kHz, to be compared with the fit of Paper I which had a standard deviation of 172 kHz when all lines were included.

In the course of the fitting a strong correlation between the values of the ground state rotational constant B_0, of the Coriolis interaction constant ζ, and the band frequency origin of the ν_3 mode was found. The second derivative of S along the appropriate direction was found to be not exactly equal to zero but was so small that it resulted in rather big confidence intervals of the above molecular parameters.

In the frame of the first-order Hamiltonian the correlation between the values of the ground state rotational constant, the Coriolis interaction constant, and the band origin frequency of the ν_3 mode follows from the spherical symmetry of the Hamiltonian. The spherical symmetry of the first-order Hamiltonian and the spherical symmetry of the dipole interaction of the ν_3 band with the resonant radiation results in the approximate selection rule for the vibration–rotation transitions of fundamental ν_3 band (*1*),

$$\Delta R = 0; \quad \Delta C = 0; \quad \Delta n = 0, \qquad [37]$$

which seriously restricts the number of strong transitions and as a consequence leads to the main ambiguity in the restoration of the parameters of the model vibration–rotation Hamiltonian from the frequencies of such transitions.

To explain the existence of the correlation between the values of the ground state rotational constant, the Coriolis interaction constant, and the band frequency of the ν_3 band, let us consider the contributions of appropriate terms of the vibra-

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tion–rotation Hamiltonian to the frequency of a $\Delta R = 0$ transition. The harmonic oscillator term has the form

$$H_{\text{h.o.}} = P_3^{0,0,0,0,1} \cdot O^{0,0,0,0,1} = t_{3,3}^{0(0,A_1)} \cdot T_{3,3}^{0(0,A_1)} \quad [38]$$

in the frameworks of the spherical tensor and of the cubic tensor formalisms, respectively. The rigid-rotor and the Coriolis interaction terms are

$$H_{\text{r.r.}} = P_0^{2,0,0,0,1} \cdot R_{A_1,1}^{2(0)} = t_0^{2(0,A_1)} \cdot T_0^{2(0,A_1)} \quad [39]$$

$$H_{\text{C.i.}} = P_3^{1,1,1,0,1} \cdot O^{1,1,1,0,1} = t_{3,3}^{1(1,F_1)} \cdot T_{3,3}^{1(1,F_1)}. \quad [40]$$

The derivation of the matrix elements in the cubic tensor formalism yields the following results

$$\langle v_3 = 0|T_0^{2(0,A_1)}|v_3 = 0\rangle = J''(J'' + 1) \quad [41]$$

with $R'' = J''$

$$\langle v_3 = 1|T_0^{2(0,A_1)}|v_3 = 1\rangle = J'(J' + 1) \quad [42]$$

$$\langle v_3 = 1|T_{3,3}^{0(0,A_1)}|v_3 = 1\rangle = 1 \quad [43]$$

$$\langle v_3 = 1|T_{3,3}^{1(1,F_1)}|v_3 = 1\rangle \sim J'(J' + 1) - R'(R' + 1) - 2. \quad [44]$$

The allowed transitions are $\Delta R = 0 \Rightarrow R' = R'' = J''$ and this results for each operator in the following contribution to the frequency:

$$f(T_0^{2(0,A_1)}) = J'(J' + 1) - R'(R' + 1) \quad [45]$$

$$f(T_{3,3}^{0(0,A_1)}) = 1 \quad [46]$$

$$f(T_{3,3}^{1(1,F_1)}) \sim J'(J' + 1) - R'(R' + 1) - 2. \quad [47]$$

So it is easy to see that the contributions to the frequencies of the $\Delta R = 0$ transitions are not independent.

The correlation between the values of the ground state rotational constant, the Coriolis interaction constant, and the band origin frequency of ν_3 band will be changed if higher order terms are taken into account. The conclusion of the numerical analysis is that the higher order terms do not destroy this correlation completely but give a tiny increase of the second-order derivative of the mean-square deviation along the direction of correlation.

The second observation in the course of preliminary computer calculations was that the ordering scheme of Hamiltonian parameters does not follow the geometrical progression with the increase of the power of the rotational operators Ω. This progression was expected from the analysis of the parameters of the third-order Hamiltonian. The decrease of the Hamiltonian parameter with increasing Ω is mainly governed by the ratio $\epsilon^2 = B/\omega$, where B is the rotational constant and ω is the characteristic vibrational frequency. Taking $B = 0.1\ \text{cm}^{-1}$ and the lowest vibrational frequency $\omega = 350\ \text{cm}^{-1}$, we get an estimate of $\epsilon^2 = 1/3500$. This is in a good agreement with the observed ordering up to $\Omega = 3$ with an ordering parameter $\epsilon^2 \sim 1/3000$. One could expect that the parameters of the $\nu_3 = 1$ state might be on the order of $3 \cdot 10^{-12}\ \text{cm}^{-1}$ in the case of $\Omega = 4$ and on the order of $10^{-15}\ \text{cm}^{-1}$ in the case of $\Omega = 5$, but our fitting confirmed the results obtained in (*1*) that the parameters with $\Omega = 5$ are appreciably higher in order of magnitude and some even higher in the case of $\Omega = 4$.

We see two reasons why the ordering scheme of molecular parameters can be broken when $\Omega \geq 4$. First, there is the fundamental question of the contribution of nonadiabatic interactions between electronic, vibrational, and rotational degrees of freedom of a molecules. As was pointed out in Ref. (*13*), the nonadiabatic terms can give an appreciable contribution to the Hamiltonian terms of order higher than three.

Second, the $\nu_3 = 1$ state is not well isolated. Owing to the Coriolis splitting of J level into $R = J - 1$, $R = J$, and $R = J + 1$ sublevels, the last of these is coming into resonance with the $\nu_2 + \nu_6$ vibrational state with increasing J, while the first is coming into resonance with the $\nu_5 + \nu_6$ vibrational state. One could expect that the avoided crossing will be at J values of about 200. So, a slow convergence of the effective Hamiltonian could be expected in the high J region of the $\nu_3 = 1$ state vibration–rotation spectrum. One can expect that the ordering parameter κ of the power expansion of Hamiltonian in this case must correspond to the critical value of $J_{\text{crit}} \approx 200$ as $\kappa \sim 1/J_{\text{crit}} \approx 5 \cdot 10^{-3}$. This value is in a good agreement with the ordering of the parameters of the tenth-order Hamiltonian when $\Omega > 4$.

The fifth-order Hamiltonian with the corrected parameters was then used to calculate the frequencies of all lines presented in Table 1. For the lines with high J values we observed big differences between measured and calculated frequencies. The differences reach 10 MHz at J values of about 90 for some lines and have a decreasing magnitude with the decreasing J values. It demonstrates that the fifth-order Hamiltonian is not adequately precise in the region of high J values to calculate the frequencies of the observed rotational transitions of the ν_3 band of SF_6 with an accuracy of a few kilohertz.

3.2. *Tenth-Order Hamiltonian*

The model Hamiltonian in the framework of the spherical tensor formalism was expanded up to higher orders in Ω. It was found that the tenth-order Hamiltonian is accurate enough to fit all the measured frequencies. It was also found that there are very strong correlations between the parameters of the ground state Hamiltonian and those of the $\nu_3 =$

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TABLE 5
Values of the 52 Adjusted Parameters of the Tenth-Order Hamiltonian

$P_3^{\Omega,K,L,k,i}$	Value in cm^{-1}	SD in cm^{-1}	$P^{(5)}$ in cm^{-1}
$P_0^{2,0,0,0,1}$	$9.1077 \cdot 10^{-2}$		$9.10772329648420 \cdot 10^{-2}$
$P_0^{4,0,0,0,1}$	$-6.5 \cdot 10^{-9}$		$-6.53975417115586 \cdot 10^{-9}$
$P_0^{4,4,0,4,1}$	$2.0 \cdot 10^{-9}$		$2.15125750188997 \cdot 10^{-9}$
$P_0^{6,0,0,0,1}$	$0*$		$-1.33190977150959 \cdot 10^{-15}$
$P_0^{6,4,0,4,1}$	$0*$		$4.15785405817911 \cdot 10^{-13}$
$P_0^{6,6,0,6,1}$	$0*$		$3.75449262106023 \cdot 10^{-15}$
$P_3^{0,0,0,0,1}$	948.10250829013857	$6.38 \cdot 10^{-9}$	948.10250872341051
$P_3^{1,1,1,0,1}$	0.308948122083929	$1.88 \cdot 10^{-9}$	0.308948411139920
$P_3^{2,0,0,0,1}$	$-1.31054157638548 \cdot 10^{-4}$	$2.06 \cdot 10^{-11}$	$-1.31056832667916 \cdot 10^{-4}$
$P_3^{2,2,2,0,1}$	$2.05109870019838 \cdot 10^{-4}$	$1.20 \cdot 10^{-10}$	$2.05098249212427 \cdot 10^{-4}$
$P_3^{2,2,2,4,1}$	$4.11278819765671 \cdot 10^{-4}$	$1.64 \cdot 10^{-10}$	$4.11294155814908 \cdot 10^{-4}$
$P_3^{3,1,1,0,1}$	$-8.86807304783516 \cdot 10^{-8}$	$3.25 \cdot 10^{-12}$	$-8.77928328347065 \cdot 10^{-8}$
$P_3^{3,3,1,4,1}$	$5.26153684327288 \cdot 10^{-9}$	$2.50 \cdot 10^{-12}$	$3.55729887941266 \cdot 10^{-9}$
$P_3^{4,0,0,0,1}$	$-4.73509558034092 \cdot 10^{-11}$	$2.23 \cdot 10^{-14}$	$-4.47660971891807 \cdot 10^{-11}$
$P_3^{4,2,2,0,1}$	$1.18000603961779 \cdot 10^{-10}$	$1.49 \cdot 10^{-13}$	$1.39841519126083 \cdot 10^{-10}$
$P_3^{4,2,2,4,1}$	$3.91696260544899 \cdot 10^{-11}$	$2.09 \cdot 10^{-13}$	$3.35619465217131 \cdot 10^{-11}$
$P_3^{4,4,0,4,1}$	$-1.04847277866846 \cdot 10^{-10}$	$4.77 \cdot 10^{-14}$	$-9.91984880735960 \cdot 10^{-11}$
$P_3^{4,4,2,4,1}$	$0*$		$0*$
$P_3^{4,4,2,6,1}$	$6.49559437805747 \cdot 10^{-11}$	$1.19 \cdot 10^{-13}$	$7.44765478079828 \cdot 10^{-11}$
$P_3^{5,1,1,0,1}$	$-9.44282102752591 \cdot 10^{-13}$	$1.65 \cdot 10^{-15}$	$-1.29183161613813 \cdot 10^{-12}$
$P_3^{5,3,1,4,1}$	$1.05476023348960 \cdot 10^{-12}$	$2.26 \cdot 10^{-15}$	$-2.11453724797371 \cdot 10^{-12}$
$P_3^{5,5,1,4,1}$	$0*$		$0*$
$P_3^{5,5,1,6,1}$	$-7.37542849003755 \cdot 10^{-13}$	$1.50 \cdot 10^{-15}$	$-8.67536690646027 \cdot 10^{-13}$
$P_3^{6,0,0,0,1}$	$-4.81692740571374 \cdot 10^{-16}$	$9.12 \cdot 10^{-18}$	$-1.51449075283739 \cdot 10^{-15}$
$P_3^{6,2,2,0,1}$	$5.76794540671468 \cdot 10^{-15}$	$6.28 \cdot 10^{-17}$	
$P_3^{6,2,2,4,1}$	$-3.91441220996698 \cdot 10^{-16}$	$8.49 \cdot 10^{-17}$	
$P_3^{6,4,0,4,1}$	$-3.36958204289256 \cdot 10^{-15}$	$2.61 \cdot 10^{-17}$	$-5.14782668704064 \cdot 10^{-15}$
$P_3^{6,4,2,4,1}$	$0*$		
$P_3^{6,4,2,6,1}$	$-1.32349033022478 \cdot 10^{-15}$	$9.26 \cdot 10^{-17}$	
$P_3^{6,6,0,6,1}$	$1.38682418938680 \cdot 10^{-15}$	$1.36 \cdot 10^{-17}$	$4.11252777187521 \cdot 10^{-15}$
$P_3^{6,6,0,6,1}$	$1.38682418938680 \cdot 10^{-15}$	$1.36 \cdot 10^{-17}$	
$P_3^{6,6,2,4,1}$	$0*$		
$P_3^{6,6,2,6,1}$	$0*$		
$P_3^{6,6,2,8,1}$	$-2.59821622852989 \cdot 10^{-15}$	$1.96 \cdot 10^{-17}$	
$P_3^{7,1,1,0,1}$	$-1.69080947280811 \cdot 10^{-17}$	$3.09 \cdot 10^{-19}$	
$P_3^{7,3,1,4,1}$	$3.43369073211348 \cdot 10^{-17}$	$5.44 \cdot 10^{-19}$	
$P_3^{7,5,1,4,1}$	$0*$		
$P_3^{7,5,1,6,1}$	$-1.48882800759839 \cdot 10^{-17}$	$5.27 \cdot 10^{-19}$	
$P_3^{7,7,1,6,1}$	$0*$		
$P_3^{7,7,1,8,1}$	$-1.21315287526588 \cdot 10^{-17}$	$1.51 \cdot 10^{-19}$	
$P_3^{8,0,0,0,1}$	$-1.23704363087576 \cdot 10^{-19}$	$1.48 \cdot 10^{-21}$	
$P_3^{8,2,2,0,1}$	$-3.90840830146077 \cdot 10^{-19}$	$1.04 \cdot 10^{-20}$	
$P_3^{8,2,2,4,1}$	$9.19191591404426 \cdot 10^{-19}$	$1.39 \cdot 10^{-20}$	
$P_3^{8,4,0,4,1}$	$2.91876714728762 \cdot 10^{-19}$	$4.92 \cdot 10^{-21}$	
$P_3^{8,4,2,4,1}$	$0*$		
$P_3^{8,4,2,6,1}$	$4.18719699100031 \cdot 10^{-20}$	$2.17 \cdot 10^{-20}$	
$P_3^{8,6,0,6,1}$	$2.83272948763298 \cdot 10^{-19}$	$4.85 \cdot 10^{-21}$	
$P_3^{8,6,2,4,1}$	$0*$		
$P_3^{8,6,2,6,1}$	$0*$		
$P_3^{8,6,2,8,1}$	$-3.80170578728490 \cdot 10^{-19}$	$7.95 \cdot 10^{-21}$	
$P_3^{8,8,0,8,1}$	$-1.51983414747677 \cdot 10^{-19}$	$1.85 \cdot 10^{-21}$	
$P_3^{8,8,2,6,1}$	$0*$		
$P_3^{8,8,2,8,1}$	$0*$		
$P_3^{8,8,2,9,1}$	$0*$		
$P_3^{8,8,2,10,1}$	$-1.41827271592883 \cdot 10^{-19}$	$6.04 \cdot 10^{-21}$	

Note. The parameters of the ground vibrational state were fixed. The parameters marked by an asterisk were fixed to zero. $P^{(5)}$ gives the value of the parameter obtained by fitting of the 136 lines of paper I with the fifth order Hamiltonian.

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TABLE 5—*Continued*

$P_3^{\Omega,K,L,k,i}$	Value in cm^{-1}	SD in cm^{-1}
$P_3^{9,1,1,0,1}$	$-7.79787039571326 \cdot 10^{-22}$	$1.88 \cdot 10^{-23}$
$P_3^{9,3,1,4,1}$	$3.94931885066651 \cdot 10^{-22}$	$3.85 \cdot 10^{-23}$
$P_3^{9,5,1,4,1}$	$0*$	
$P_3^{9,5,1,6,1}$	$-1.65142713864744 \cdot 10^{-21}$	$4.73 \cdot 10^{-23}$
$P_3^{9,7,1,6,1}$	$0*$	
$P_3^{9,7,1,8,1}$	$4.52279216670969 \cdot 10^{-22}$	$2.58 \cdot 10^{-23}$
$P_3^{9,9,1,8,1}$	$0*$	
$P_3^{9,9,1,9,1}$	$0*$	
$P_3^{9,9,1,10,1}$	$1.61505464654277 \cdot 10^{-21}$	$2.83 \cdot 10^{-23}$
$P_3^{10,0,0,0,1}$	$5.53232743151482 \cdot 10^{-24}$	$8.14 \cdot 10^{-26}$
$P_3^{10,2,2,0,1}$	$3.45846417899763 \cdot 10^{-23}$	$5.82 \cdot 10^{-25}$
$P_3^{10,2,2,4,1}$	$-6.70306608694819 \cdot 10^{-23}$	$7.90 \cdot 10^{-25}$
$P_3^{10,4,0,4,1}$	$-3.32380242402471 \cdot 10^{-23}$	$3.04 \cdot 10^{-25}$
$P_3^{10,4,2,4,1}$	$0*$	
$P_3^{10,4,2,6,1}$	$-7.56051046929356 \cdot 10^{-23}$	$1.69 \cdot 10^{-24}$
$P_3^{10,6,0,6,1}$	$-2.27018375171350 \cdot 10^{-23}$	$4.17 \cdot 10^{-25}$
$P_3^{10,6,2,4,1}$	$0*$	
$P_3^{10,6,2,6,1}$	$0*$	
$P_3^{10,6,2,8,1}$	$1.66446174645650 \cdot 10^{-22}$	$2.50 \cdot 10^{-24}$
$P_3^{10,8,0,8,1}$	$3.39521523588953 \cdot 10^{-23}$	$2.82 \cdot 10^{-25}$
$P_3^{10,8,2,6,1}$	$0*$	
$P_3^{10,8,2,8,1}$	$0*$	
$P_3^{10,8,2,9,1}$	$0*$	
$P_3^{10,8,2,10,1}$	$2.53651169450046 \cdot 10^{-22}$	$6.32 \cdot 10^{-24}$
$P_3^{10,10,0,10,1}$	$-2.92659250809426 \cdot 10^{-23}$	$1.16 \cdot 10^{-25}$
$P_3^{10,10,2,8,1}$	$0*$	
$P_3^{10,10,2,9,1}$	$0*$	
$P_3^{10,10,2,10,1}$	$0*$	
$P_3^{10,10,2,12,1}$	$-5.56005946525859 \cdot 10^{-22}$	$1.11 \cdot 10^{-23}$
$P_3^{10,10,2,12,2}$	$2.74870384650695 \cdot 10^{-22}$	$5.41 \cdot 10^{-24}$

1 state Hamiltonian. These correlations were again attributed to the fact that only $\Delta R = 0$ transition frequencies were measured in the experiment. Thus it was not possible to make unambiguous conclusions about the ordering scheme of the Hamiltonian of the ground vibrational state which is free of resonances with any combination vibration state. In the case of the ground state Hamiltonian it would be possible to trace the contribution of the nonadiabatic terms. At this point we cut the expansion of the ground state Hamiltonian at the fourth order in Ω and fixed all the parameters to the most reliable values known from literature up to date (see the recent papers (*19–22*)). Unfortunately IR high-resolution spectroscopy is not free from the disadvantage that concerns the correlation of the ground vibration state parameters and the excited vibration state parameters due to the contact transformation invariance of the Hamiltonian and to the lack of comprehensive information on forbidden transitions. The most straightforward and reliable way to get unambiguous data on the rotation parameters of the ground vibrational state of SF_6 might be magnetic dipole spectroscopy of rotational transitions in the ground vibrational state (*23*, *24*).

The results of the fitting obtained with fixed parameters for the ground state Hamiltonian and the $\nu_3 = 1$ state Hamiltonian expanded to tenth order in Ω in the frame of the spherical tensor formalism are presented in Tables 1 and 5. The values of the parameters were not rounded in accordance with the common rules to the digit which corresponds to the order of magnitude of the standard deviation (SD) of the parameter. In our case we see that the standard deviation of a parameter defined mainly by the correlations between the large number of parameters and the common rounding procedure would yield values too rough for the parameters. We intentionally present unrounded values in order for everyone to be able to use our parameters to simulate the frequencies of vibration–rotation transitions of the ν_3 fundamental band with an accuracy estimated here to 40 kHz up to $J \sim 100$. Also we hope that it will be possible in the near future to measure the high-resolution spectra of the so-called forbidden ($\Delta R \neq 0$) vibration–rotation transitions of the ν_3 fundamental band and thus to break the correlations between spectroscopic parameters. In this case the unrounded values would be very useful as the starting point for the subsequent refinement of the parameters.

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4. CONCLUSIONS

This paper presents a very complete set of accurate experimental data for the ν_3 band of SF_6: 321 frequencies of the P, Q, and R branches with J values ranging from 3 to 96 have been measured with an accuracy of a few kilohertz (unfortunately limited in some cases by the unresolved hyperfine structure and by the hyperfine coupling within superfine clusters). To achieve an analysis of such a set of data, we have found it necessary to expand the Hamiltonian up to the tenth order. This is because of the slow convergence of the power expansion of the Hamiltonian in the range of high J values. It is the first time that an expansion is performed to that order. This expansion has been done using two different tensorial formalisms, the first one through tensor coupling algebra in $O(3)$ and the second one in O_h. These two expressions of the Hamiltonian have been compared analytically. The relations between both sets of parameters are given up to sixth order. They have also been compared numerically and this comparison gives results which do not differ by more than the precision of computers. Thanks to the analytical comparison, the risk of error in writing the operators is very small and thanks to the numerical comparison, the risk of error in the programmation of the calculus is almost zero. Even if the comparisons have been performed only to sixth order (Table 3), the FORTRAN program packages have been developed for both formalisms so as to provide an expansion up to any order. The expressions of the matrix elements are written independently of the order. As a consequence the quality of the analyzed data and of the model allow us to state that the predicted frequencies (over 40 000 allowed lines for $J < 100$) are very accurate. In the past, every time that a new predicted line was measured the agreement was better than 40 kHz even for the highest J values. These predicted frequencies can be used as frequency references in spectral regions where frequency measurements are lacking and will be sent upon request to anyone interested. These results will be especially useful to predict intensities and to model the band absorption. Indeed, the SF_6 molecule is now used extensively in industry as an isolator (in transformers, high voltage cables, etc.) and this molecule has been detected in the atmosphere. The increase of its concentration (doubling every 10 years) is such that it has become essential to follow its evolution. On the other hand, our results can be used for further studies of the Born–Oppenheimer approximation or of interacting bands such as ν_3 with $\nu_2 + \nu_6$ or ν_3 with $\nu_5 + \nu_6$.

The hyperfine and superfine structures of all the lines presented here has been recorded and compared with theory (*5*, *6*) with a very good quantitative agreement (except, as mentioned in the introduction, for the differential saturation effects in the unresolved structures, in which case only a qualitative agreement could be obtained with the predictions of the weak-field theory). These structures will be displayed in a future publication.

With the technology and equipment available today to increase the tunability of CO_2 lasers, it is possible to record any line in this ν_3 band spectrum with subkilohertz resolution and to perform an absolute frequency measurement of any of its hyperfine components with a few hertz accuracy, the only limitation being the time that one is willing to spend on this project. But now, the main direction of progress to achieve our initial goal to test the Hamiltonian and to obtain physical rather than effective constants would be a better knowledge of the ground vibrational state. This could be achieved through a measurement of forbidden lines or even through a direct study of rotational magnetic dipole transitions (*23*, *24*) induced by a microwave field with optical preparation and detection of the populations in a molecular beam.

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