

3.2.3 Non-linear triatomic radicals

3.2.3.1 Preliminary remarks

1 Introduction

The Hamiltonian used to describe the microwave spectra of non-linear molecules in open-shell electronic states can be written as the sum of several separate terms:

$$H = H_{\text{rot}} + H_{\text{cd}} + H_{\text{ss}} + H_{\text{sr}} + H_{\text{srd}} + H_{\text{hfs}} + H_{\text{Q}} + H_{\text{Z}}.$$

The individual terms in this effective Hamiltonian are taken to have the following form:

H_{rot} Rigid asymmetric rotor Hamiltonian

The rigid rotor Hamiltonian for a molecule in vibrational level v is written

$$H_{\text{rot}} = A_v N_a^2 + B_v N_b^2 + C_v N_c^2$$

where A_v , B_v and C_v are the rotational “constants” and N_a , N_b and N_c are the components of the rotational angular momentum N , referred to the principal inertial axes [51Van]. The rotational constants are closely related to the principal moments of inertia

$$A_v = \hbar^2/2hI_{av}, \quad B_v = \hbar^2/2hI_{bv}, \quad C_v = \hbar^2/2I_{cv},$$

where H_{rot} , A_v , B_v and C_v are measured in frequency units, thus N_a , N_b and N_c are dimensionless. The expressions for the rotational constants may become more complicated in the non-rigid case depending on the form adopted for the corrections to the rotational energy levels for the effects of centrifugal distortion [67Wat, 77Wat2].

H_{cd} Centrifugal distortion effects

Watson [67Wat] has shown that the number of centrifugal distortion parameters which can be determined from experimental data is less than the number of independent parameters in the fundamental Hamiltonian first formulated by Kivelson and Wilson [52Kiv, 53Kiv]. It is therefore necessary to reduce the Hamiltonian so that it contains only determinable combinations of parameters (otherwise indeterminacies manifest themselves in the least-squares fitting of experimental data). Separate reductions have to be performed at the levels of the quartic, sextic, etc. terms. Two different reductions have become generally accepted, called the symmetric (S) and asymmetric (A) reduction by Watson. The former is particularly appropriate to molecules with inertial properties near either the oblate or prolate symmetric top limits whereas the latter is better suited to describe the energy levels of strongly asymmetric rotors. The A-reduced Hamiltonian has the advantage that its matrix representation is simpler but its parameters do not correlate smoothly with those in the symmetric top limit.

The A-reduced form for the quartic and sextic centrifugal distortion terms is

$$\begin{aligned} H_{\text{cd}}^{\text{A}} = & -\Delta_N (\mathbf{N}^2)^2 - \Delta_{NK} \mathbf{N}^2 N_z^2 - \Delta_K N_z^4 - \frac{1}{2} [\delta_N \mathbf{N}^2 + \delta_K N_z^2, (N_+^2 + N_-^2)]_+ \\ & + \Phi_N (\mathbf{N}^2)^3 + \Phi_{NK} (\mathbf{N}^2)^2 N_z^2 + \Phi_{KN} \mathbf{N}^2 N_z^4 + \Phi_K N_z^6 \\ & + \frac{1}{2} [\phi_N (\mathbf{N}^2)^2 + \phi_{NK} \mathbf{N}^2 N_z^2 + \phi_K N_z^4, (N_+^2 + N_-^2)]_+. \end{aligned}$$

The symbol $[A, B]_+$ stands for the anti-commutator $(AB+BA)$ and the operator N_{\pm} is defined by

$$N_{\pm} = (N_x \pm iN_y).$$

Following Watson [77Wat2] the sextic coefficients have been denoted ϕ_N, \dots, ϕ_K rather than the previous H_N, \dots, h_K [68Wat] because it seems preferable to reserve the latter for the corresponding terms of the symmetric top reduced Hamiltonian.

The symmetric top or S-reduced Hamiltonian for quartic and sextic centrifugal distortion terms has the form

$$\begin{aligned} H_{\text{cd}}^{\text{S}} = & -D_N (\mathbf{N}^2)^2 - D_{NK} \mathbf{N}^2 N_z^2 - D_K N_z^4 + d_1 \mathbf{N}^2 (N_+^2 + N_-^2) + d_2 (N_+^4 + N_-^4) \\ & + H_N (\mathbf{N}^2)^3 + H_{NK} (\mathbf{N}^2)^2 N_z^2 + H_{KN} \mathbf{N}^2 N_z^4 + H_K N_z^6 \\ & + h_1 (\mathbf{N}^2)^2 (N_+^2 + N_-^2) + h_2 \mathbf{N}^2 (N_+^4 + N_-^4) + h_3 (N_+^6 + N_-^6). \end{aligned}$$

Watson [77Wat1, 77Wat2] has given the relationships between the parameters in the A and S reduced Hamiltonians. It is thus possible to estimate the parameters for the alternative reduction from those determined in a particular fit to experimental data. Note that the values determined for the rotational constants also depend on the reduction employed.

In the fit of some data sets for light molecules which display large centrifugal distortion effects, it has been necessary to include the leading octic terms also. In the present compilation, these effects are described by

$$H_{\text{cd}}^{(8)} = L_K N_z^8 + \dots$$

The rotor problem can be treated choosing different quantization axes. For near prolate tops the so-called I^r representation, $a \leftrightarrow z, b \leftrightarrow x, c \leftrightarrow y$ is appropriate, while in the oblate case the choice $z \leftrightarrow c$ is preferable [63All].

H_{ss} Electronic spin-spin (dipolar) interaction

The effective spin dipolar Hamiltonian for asymmetric top molecules has been derived by Van Vleck [51Van]:

$$\begin{aligned} H_{\text{ss}} = & \alpha (3S_z^2 - \mathbf{S}^2) + \beta (S_x^2 - S_y^2) + \gamma (S_x S_y + S_y S_x) \\ & + \delta (S_x S_z + S_z S_x) + \varepsilon (S_y S_z + S_z S_y). \end{aligned}$$

Symmetry arguments can be used to show that only the parameters α and β are non-zero for the symmetric triatomic molecule AB_2 ; only one of the three other parameters (δ for the I^r representation) is non-zero for the non-symmetric molecule ABC .

H_{sr} Electronic spin-rotation interaction

The effective spin-rotation Hamiltonian for asymmetric top molecules has been discussed by several authors [51Van, 61Cur, 79Bro]. In general it takes the form

$$H_{\text{sr}} = \frac{1}{2} \sum_{\alpha, \beta} \varepsilon_{\alpha\beta} (N_{\alpha} S_{\beta} + S_{\beta} N_{\alpha})$$

where the indices α and β run separately over the molecule-fixed coordinates x, y, z , and $\varepsilon_{\alpha\beta}$ are the spin-rotation parameters. There are in principle nine independent components of the spin rotation tensor but not all of them are determinable in practice. In the same way that the rotational and centrifugal distortion Hamiltonians can be reduced so that they are expressed in terms of determinable parameters only [67Wat], the spin-rotation Hamiltonian must be reduced by application of appropriate transformations in spin space. A solution to this problem has been given by Brown and Sears [79Bro], who show that there are at the most six determinable parameters. If we restrict ourselves to triatomic molecules, the situation is even simpler. For an AB_2 molecule with C_{2v} symmetry, the Hamiltonian is

$$H_{\text{sr}} = \varepsilon_{aa} N_a S_a + \varepsilon_{bb} N_b S_b + \varepsilon_{cc} N_c S_c$$

where a , b , and c are the principal axes of the inertial tensor (defined by symmetry). The ABC molecule has only one element of symmetry, the plane of reflection (C_s); the spin-rotation Hamiltonian is a little more complicated in this case. The preferred form [79Bro] is:

$$H_{\text{sr}} = \tilde{\varepsilon}_{aa} N_a S_a + \tilde{\varepsilon}_{bb} N_b S_b + \tilde{\varepsilon}_{cc} N_c S_c + \frac{1}{2} \tilde{\varepsilon}_{ab} ([N_a, S_b]_+ + [N_b, S_a]_+)$$

where $\tilde{\varepsilon}_{aa}, \tilde{\varepsilon}_{bb}$, etc. are reduced parameters, related to $\varepsilon_{\alpha\beta}$ as shown by Brown and Sears.

H_{srd} The centrifugal distortion corrections to the spin-rotation interaction

The spin-rotation interaction is modified by centrifugal distortion effects in much the same way as the rotational kinetic energy is altered. Such effects have been discussed by Dixon and Duxbury [67Dix] and by Brown and Sears [77Bro, 79Bro]. In particular, the latter authors have considered the reduction of the quartic terms in the Hamiltonian so that only determinable combinations of parameters are retained. There are 6 quartic parameters for a C_{2v} molecule (AB_2) and 8 for a C_s molecule (ABC). Brown and Sears [79Bro] give two possible reduced forms, constructed along the same lines as Watson's A- and S-reduced Hamiltonians for rotational motion.

The A-reduced form for C_{2v} molecules is

$$H_{\text{srd}}^A = \Delta_N^s N^2 (N \cdot S) + \frac{1}{2} \Delta_{NK}^s [N^2, N_z S_z]_+ + \Delta_{KN}^s N_z^2 (N \cdot S) + \Delta_K^s N_z^3 S_z \\ + \delta_N^s (N \cdot S) (N_+^2 + N_-^2) + \frac{1}{2} \delta_K^s [N_z S_z, (N_+^2 + N_-^2)]_+,$$

where the coefficients have been defined by analogy with the corresponding coefficients in H_{cd} (note however the change of sign in this definition). The S-reduced form for C_{2v} molecules is

$$H_{\text{srd}}^S = D_N^s N^2 (N \cdot S) + \frac{1}{2} D_{NK}^s [N^2, N_z S_z]_+ + D_{KN}^s N_z^2 (N \cdot S) + D_K^s N_z^3 S_z \\ + d_1^s (N_+^2 + N_-^2) (N \cdot S) + d_2^s (N_+^3 S_+ + N_-^3 S_-).$$

Brown and Sears [79Bro] have given the relationships between these parameters and the parameters $\eta_{\alpha\beta\gamma\delta}$ involved in the basic definition of centrifugal distortion corrections to the spin-rotation interaction.

H_{hfs} Magnetic nuclear hyperfine interactions

There are two contributions to the magnetic hyperfine interaction for each nucleus.

$$H_{\text{hfs}} = H_{\text{FC}} + H_{\text{dip}}.$$

These are the Fermi contact and dipolar interactions respectively. The Fermi contact term describes the isotropic interaction

$$H_{\text{FC}} = (O)_I \mathbf{I} \cdot \mathbf{S}$$

where

$$(O)_I = -2\mu_B g_N \mu_N / (3\mu_0^{-1}) \sum_i g_i \langle \delta(r_i) \rangle,$$

g_N and g_i are the nuclear and electron spin g -factors, μ_N and μ_B are the nuclear and Bohr magnetons, μ_0 is the permeability of free space and $\langle \delta(r_i) \rangle$ gives the electron density at the nucleus for electron i . The summation is performed over unpaired electrons only.

The dipolar interaction is anisotropic and can be represented in terms of the components of a cartesian tensor $(\alpha\beta)_l$, often written as $T_{\alpha\beta}$:

$$H_{\text{dip}} = \sum_{\alpha\beta} (\alpha\beta)_l S_\alpha I_\beta,$$

where α, β run separately over the cartesian coordinates a, b , and c . The tensor components can, to a good approximation, be interpreted as the expectation values

$$(\alpha\beta)_l = \frac{\mu_B g_N \mu_N}{4\pi\mu_0^{-1}} \sum_i g_i \langle (\delta_{\alpha\beta} - 3\mathbf{e}_\alpha \mathbf{e}_\beta) / r_i^3 \rangle$$

where the summation again runs over open shell electrons only, $\delta_{\alpha\beta}$ is the Kronecker delta symbol, \mathbf{e}_α and \mathbf{e}_β are unit vector components along the principal axes α and β and r_i is the distance from the given nucleus to electron i . The operator inside the expectation value is often expressed in terms of spherical polar coordinates (r_i, θ_i, ϕ_i) . For example, it becomes $\langle (1 - 3\cos^2 \theta_i) / r_i^3 \rangle$ for the component $(zz)_l$.

There is a pair of terms of the above form for each nucleus with non-zero spin present in the molecule. As before, symmetry can be used to reduce the number of non-zero components of the traceless tensor $(\alpha\beta)_l$. For a C_{2v} molecule (AB_2) with a single non-zero spin nucleus there are 3 non-zero components $(aa)_l, (bb)_l, (cc)_l$, of which 2 are independent since $(aa)_l + (bb)_l + (cc)_l$ equals zero. For the planar ABC molecule, the additional components $(ab)_l$ and $(ba)_l$ are non-zero. In all analyses performed so far, it has been assumed that these components are equal. It is not clear that this is so and if not, what combinations of parameters are determinable. The $(ab)_l$ component is also non-zero for an AB_2 molecule with 2 equivalent nuclei of non-zero spin. If the nuclear spins are I_1 and I_2 , the dipolar Hamiltonian is

$$H_{\text{dip}} = (aa)_l I_a S_a + (bb)_l I_b S_b + (cc)_l I_c S_c + (ab)_l [(I_1 - I_2)_a S_b + (I_1 - I_2)_b S_a]$$

where I is the total nuclear spin, $I = I_1 + I_2$. The additional term mixes ortho and para spin states. The nomenclature used here is due to Curl and Kinsey [61Cur]. In some of the tables in this section, $(\alpha\alpha)_l$ is written as $T_{\alpha\alpha}(I)$ to which it is equivalent

H_Q The nuclear electric quadrupole interaction

The interaction of the nuclear electric quadrupole with the molecular electric field gradient can be described by the product of the nuclear quadrupole moment tensor $eQ_{\alpha\beta}$ and the electric field gradient tensor $(\nabla E)_{\alpha\beta}$:

$$H_Q = eQ \cdot \nabla E$$

where $-e$ is the charge on the electron. The operator is often re-expressed in terms of the nuclear spin angular momentum operators by use of the Wigner-Eckart theorem:

$$H_Q = \sum_{\alpha\beta} (\alpha\beta)_Q I_\alpha I_\beta$$

where α, β run over the principal coordinates of inertia and $(\alpha\beta)_Q$ are the quadrupole parameters [61Cur]. This form is in some ways more convenient for the evaluation of matrix elements. For C_{2v} molecules, it reduces to

$$H_Q = (aa)_Q I_a^2 + (bb)_Q I_b^2 + (cc)_Q I_c^2$$

with $(aa)_Q + (bb)_Q + (cc)_Q = 0$. The parameters can be interpreted in terms of

$$(\alpha\beta)_Q = [eQ/2I(2I-1)] \langle \partial^2 V / \partial \alpha \partial \beta \rangle$$

where Q is the nuclear quadrupole moment. In some of the tables of this section, we use $\chi_{\alpha\beta}$ for the quadrupole coupling parameter. It is related to $(\alpha\beta)_Q$ by $(\alpha\beta)_Q = \chi_{\alpha\beta} / [2I(2I-1)]$.

H_Z Zeeman interactions

The effective Zeeman Hamiltonian for an asymmetric top molecule in an open-shell state has been given by several authors in the literature, for example Pryce [50Pry] or Bowater, Brown, and Carrington [73Bow]. The operator can be written in cartesian tensor notation as [80Eve, 00Bro]:

$$H_Z = -g_s\mu_B \mathbf{B} \cdot \mathbf{S} - g_L\mu_B \mathbf{B} \cdot \mathbf{L} - \mu_B \mathbf{B} \cdot \mathbf{g}_1 \cdot \mathbf{S} - \mu_B \mathbf{B} \cdot \mathbf{g}_r \cdot \mathbf{N} - g_N\mu_N \mathbf{B} \cdot \mathbf{I}$$

where \mathbf{B} is the applied flux density, μ_B and μ_N are the Bohr and nuclear magnetons, respectively. Of the g -factors, g_s and g_L are the isotropic spin and orbital g -factors, the second rank tensors \mathbf{g}_1 and \mathbf{g}_r describe the anisotropic spin and rotational interactions and g_N is the nuclear spin g -factor. Note that there has been a change of sign for the major g -factors, g_s and g_L , since the last volume (LB New Series II/19D2, section 3.2.2.1). This change has been made to conform to the recommendation of Brown *et al.* [00Bro] that these g -factors be defined as *negative* quantities, approximately equal to -2 and -1 , respectively. The negative sign in this convention shows that the magnetic dipole moment points in the opposite direction to the angular momentum from which it derives. Unless the molecule has a 3-fold or higher axis of symmetry (e.g. CH_3O), the orbital angular momentum is quenched and the contribution to the Zeeman effect from this source, the second term, vanishes. For the majority of problems, therefore, this term may be omitted. The anisotropic term represents the interaction between the magnetic moment arising from unquenched orbital angular momentum and the external magnetic field. The Zeeman Hamiltonian, expressed in terms of spherical tensor operators, has been given by Bowater *et al.* [73Bow]. Since the anisotropic spin tensor \mathbf{g}_1 is traceless, there are only three independent spin g -factors which are sometimes written

$$\begin{aligned} g_s^{aa} &= g_s - g_1^{aa} \\ g_s^{bb} &= g_s - g_1^{bb} \\ g_s^{cc} &= g_s - g_1^{cc} \end{aligned}$$

Note that for molecules of lower than orthorhombic symmetry, the off-diagonal components of the tensors \mathbf{g}_1 and \mathbf{g}_r are not zero by symmetry.

Experimental data are used to determine the parameters of the appropriate molecular Hamiltonian by numerical procedures that involve the determination of the eigenvalues and eigenfunctions of the Hamiltonian. The matrix elements required have been given in many places in the literature [61Cur, 71God, 73Bow, 77Wat2, 79Bro]. There are some mathematical and computational advantages in using spherical tensor techniques. A simple procedure for dealing with several nuclear spins has been described by Godfrey [71God]. Three different types of angular momentum are involved (\mathbf{N} , \mathbf{S} , and \mathbf{I}) and they can interact through a variety of coupling schemes. However, in almost every case studied so far, the spin-rotation interaction is larger than the hyperfine effects so that natural scheme to use in the basis sets is

$$\mathbf{N} + \mathbf{S} = \mathbf{J}, \quad \mathbf{J} + \mathbf{I} = \mathbf{F}.$$

The quantum number J remains good enough that it can be unambiguously defined: it is used to label the fine structure transitions in the following tables. The situation becomes more complicated when two or more nuclear spins are involved. For the coupling of two nuclear spins to \mathbf{J} it is usual to define an intermediate angular momentum \mathbf{F}_1

$$\mathbf{J} + \mathbf{I}_1 = \mathbf{F}_1, \quad \mathbf{F}_1 + \mathbf{I}_2 = \mathbf{F}.$$

Again, if the first spin is much more strongly coupled than the second, the quantum number F_1 remains good and can be used to label the levels involved in the transitions. However, it often happens that the two hyperfine interactions are of similar magnitude and F_1 is not well-defined. In this case, the fine and

hyperfine substates of a given rotational level ($N_{K_a K_c}$) with the same value of F are identified by an energy ordering index i : the index increases with energy so that the lowest state has $i = 1$. Such a definition is consistent with that adopted for labeling the electron spin fine structure states in molecules [66Her].

In quoting the results of fits of experimental data to a Hamiltonian, it is important to specify the representation employed (usually I^r for a molecule nearer the prolate symmetric top limit and III^r or III^r for a molecule near the oblate limit) and the reduction(s) used in the centrifugal distortion and spin-rotation Hamiltonians (A or S in the present compilation).

A formulation of the Hamiltonian for an asymmetric top molecule in an open shell state in spherical tensor notation has been given by Bowater, Brown, and Carrington [73Bow]. This has been reproduced in the book by Hirota [85Hir]. Details of a computer program based on this formulation have been given by Sears [84Sea1, 84Sea2]. This program is available in the public domain.

2 List of tabulated parameters

A, B, C	rotational constants for an asymmetric rotor in a given vibrational state; the subscripts v have been omitted in the tables since the vibrational state is shown separately
Δ_c	inertial defect with respect to the c axis, $I_{cc} - I_{aa} - I_{bb}$
$\Delta_N, \Delta_{NK}, \Delta_K, \delta_N, \delta_K$	quartic centrifugal distortion parameters in an A-reduced Hamiltonian ^{a)}
$\Phi_N, \Phi_{NK}, \Phi_{KN}, \Phi_K, \phi_N, \phi_{NK}, \phi_K$	sextic centrifugal distortion parameters in an A-reduced Hamiltonian ^{a)}
$\Lambda_N, \Lambda_{NNK}, \Lambda_{NK}, \Lambda_{KKN}, \Lambda_K, \lambda_N, \lambda_{NK}, \lambda_{KN}, \lambda_K$	octic centrifugal distortion parameters in an A-reduced Hamiltonian ^{a)}
$D_N, D_{NK}, D_K, d_1, d_2$	quartic centrifugal distortion parameters in an S-reduced Hamiltonian ^{a)}
$H_N, H_{NK}, H_{KN}, H_K, h_1, h_2, h_3$	sextic centrifugal distortion parameters in an S-reduced Hamiltonian ^{a)}
$L_N, L_{NNK}, L_K, L_{KKN}, L_{NK}, l_1, l_2, l_3, l_4$	octic centrifugal distortion parameters in an S-reduced Hamiltonian ^{a)}
α, β	electronic spin-spin dipolar parameters
$\mathcal{E}_{aa}, \mathcal{E}_{bb}, \mathcal{E}_{cc}$	electron spin-rotation parameters for a C_{2v} molecule
$\tilde{\mathcal{E}}_{aa}, \tilde{\mathcal{E}}_{bb}, \tilde{\mathcal{E}}_{cc}, \tilde{\mathcal{E}}_{ab}$	reduced electron spin-rotation parameters for a non-symmetric triatomic molecule (C_s)
$\mathcal{A}_N^s, \mathcal{A}_{NK}^s, \mathcal{A}_{KN}^s, \mathcal{A}_K^s, \delta_N^s, \delta_K^s$	parameters for the quartic centrifugal distortion of the spin-rotation Hamiltonian using an A-reduction
$D_N^s, D_{NK}^s, D_{KN}^s, D_K^s, d_1^s, d_2^s$	parameters for the quartic centrifugal distortion of the spin-rotation Hamiltonian using an S-reduction
$H_K^s, h_1^s, h_2^s, h_3^s, \dots$	parameters for the sextic centrifugal distortion of the spin-rotation Hamiltonian in S-reduction; an upper index s is generally added to the c.d. symbols above to indicate the corresponding spin-rotation centrifugal distortion parameters, in both S and A reduction
$(O)_I$ or $a_F(I)$	isotropic nuclear magnetic hyperfine parameter
$(aa)_I, (bb)_I, (cc)_I, (ab)_I$	magnetic hyperfine dipolar interaction parameters, expressed in terms of the principal inertial axes

^{a)} see [77Wat2] for the definitions of these parameters; note that authors use a variety of notations for the centrifugal distortion parameters higher than quartic

$T_{aa}(I), T_{bb}(I), T_{cc}(I), T_{ab}(I)$	alternative notation for hyperfine dipolar interaction parameters
$C_{aa}(I), C_{bb}(I), C_{cc}(I)$ or $M_{aa}(I), M_{bb}(I), M_{cc}(I)$	nuclear spin-rotation parameters, see Vol.II24/C; different sign conventions are in use
$(aa)_Q, (bb)_Q, (cc)_Q$	nuclear electric quadrupole coupling parameters
$\chi_{aa}(I), \chi_{bb}(I), \chi_{cc}(I)$	alternative notation for the nuclear electric quadrupole coupling parameters
$g_s^{aa}, g_s^{bb}, g_s^{cc}$	principal components of the electron spin g-tensor
g_s	isotropic electron spin g-factor
$g_l^{aa}, g_l^{bb}, g_l^{cc}$	principal components of the anisotropic electron spin g-tensor
$g_r^{aa}, g_r^{bb}, g_r^{cc}$	principal components of the rotation g-tensor
$r_s(X - Y), r_0(X - Y), r_e(X - Y)$	substitution, effective ground state and equilibrium values of the X - Y internuclear distance
$\angle_s(XYX), \angle_0(XYX), \angle_e(XYX)$	substitution, effective ground state and equilibrium values of the XYX bond angle
$\langle \delta r \rangle_I$	density of the unpaired electron at nucleus I
$\langle 1/r^3 \rangle_I, \langle (1 - 3 \cos^2 \theta)/r^3 \rangle_I$	expectation value of the odd electron position (r, θ) with respect to nucleus I

3 List of symbols used

$\tilde{X}^2A_1, \tilde{X}^2B_1$ etc.	designation of the electronic state involved. \tilde{X} signifies the ground electronic state, \tilde{A} the first excited state and so on
ν_1, ν_2, ν_3	vibrational quantum numbers for the three normal modes of vibration. In most cases, ν_2 refers to the bending vibration
$'$, $''$	the upper state quantum numbers are indicated by a single prime ($'$), the lower states by a double prime ($''$)
N	quantum number associated with rotational angular momentum N
K_a	quantum number for rotational angular momentum component about the a axis in the limit of a prolate symmetric top
K_c	quantum number for rotational angular momentum about the c axis in the limit of an oblate symmetric top
J	quantum number associated with the resultant angular momentum obtained by coupling the rotational and electron spin angular momenta, $J = N + S$
F	quantum number associated with the total angular momentum F inclusive of all nuclear spins
F_1	quantum number associated with an intermediate angular momentum, obtained by coupling the first of two nuclear spins to J ($F_1 = J + I_1$). This quantum number is well-defined if the interaction involving I_1 is much larger than that involving I_2
i	index of energy levels with the same value of F in a particular rotational level N_{KaKc} . The index labels the states in order of increasing energy ($i = 1$ is the lowest, then $i = 2$ and so on). This index is used when the intermediate quantum numbers J and/or F_1 are not well-defined, as is the case in NF_2 , for example.

4 Arrangement of substances

- | | |
|----------------------------------|----------------------|
| 1. CH ₂ | 10. HO ₂ |
| 2. NH ₂ | 11. HS ₂ |
| 3. PH ₂ | 12. ClO ₂ |
| 4. AsH ₂ | 13. BrO ₂ |
| 5. H ₂ O ⁺ | 14. FS ₂ |
| 6. HCS | 15. ClS ₂ |
| 7. HSC | 16. CaSH |
| 8. HSiO | 17. YC ₂ |
| 9. HSiS | |

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