2.9.2 Linear and symmetric top molecules

Rotational g-values, magnetic susceptibilities and anisotropies, paramagnetic and diamagnetic contributions, molecular quadrupole moments, electronic charge distributions, spin-rotation and spin-spin coupling parameters, nuclear g-values from the rotational Zeeman effect and nuclear magnetic shielding parameters from the rotational Zeeman effect

2.9.2.1 Preliminary remarks

1. Introduction

Only in a few rotational transitions has microwave spectroscopy (MW) been able to resolve zero-field magnetic hyperfine structure (hfs) as caused by spin-rotation and spin-spin interactions. Molecular-beam methods, on the other hand, can resolve these splittings. This latter technique—be it in the form of beam-maser spectroscopy (BMS), molecular-beam magnetic resonance (MBM), molecular-beam electric resonance (MBE) and molecular-beam microwave spectroscopy (MBMS)—is only recently being applied to an ever growing number of polyatomic systems. Up to the present time, spin-rotation and spin-spin coupling tensors have been determined completely in less than ten polyatomic molecules.

With the exception of nuclear-shielding anisotropy, external-magnetic-field hfs is normally resolved by conventional MW if field strengths of more than 10 kGauss are applied. Since this simple technique is applicable to many rotational transitions in a considerable number of polar molecules most of the interaction constants entered in the following tables are of the external-magnetic-field type.

The hfs Hamiltonian may be written in tensorial form as \[ H = \sum_{k} \left( \mu_{k} \cdot M_{k} \cdot J + \left( \sigma_{k} \cdot D_{1} \cdot J \right) \right) \]

where

\[ \mu_{k} = \text{the magnetic moment of the } k\text{-th nucleus} \]

\[ g_{k} = \text{the nuclear g-factor} \]

\[ I_{k} = \text{the nuclear spin} \]

\[ J = \text{the rotational angular momentum} \]

\[ H = \text{the magnetic field strength} \]

\[ M_{k} = \text{the spin-rotation coupling tensor of the } k\text{-th nucleus} \]

\[ D_{kl} = \text{the spin-spin coupling tensor of nuclei } k \text{ and } l \]

\[ g = \text{the molecular g-tensor} \]

\[ \xi = \text{the magnetic susceptibility tensor} \]

\[ \sigma = \text{the nuclear shielding tensor} \]

\[ t = \text{conjugate transpose} \]

It is appropriate to refer these quantities to the molecular-principal-axis system \((a, b, c)\). In this way, the tensor components \(M_{k}, D_{kl}, g_{k}, \xi_{kn}, \sigma_{kn}\) become uniquely defined molecular properties \((g, g' = a, b, c)\). However, only the diagonal tensor components are useful in analysing hfs spectra as non-diagonal terms, \(g \neq g'\), do not enter diagonal matrix elements in \(J\), and higher-than-first-order perturbations in \(J\) have not been observed so far. Thus it is sufficient to consider an effective Hamiltonian diagonal in \(J\). This Hamiltonian is customarily written in terms of rotationally dependent interaction strengths \(C_{k}^{(J_{k}), (J_{k}'), (J_{k}')}\), \(D_{kl}^{(J_{k}), (J_{k}'), (J_{k}')}\), \(g(J_{k}), (J_{k}'), (J_{k}'), \xi(J_{k}), (J_{k}'), (J_{k}'), \) and \(\sigma(J_{k}), (J_{k}'), (J_{k}'), \) in the following way:

\[ H = \sum_{k} C_{k}^{(J_{k}), (J_{k}'), (J_{k}')} I_{k} \cdot J + \sum_{k \neq l} D_{kl}^{(J_{k}), (J_{k}'), (J_{k}')} \frac{1}{J(J+1)} \left\{ \frac{3}{2} [(I_{k} \cdot J)(I_{k}' \cdot J) + (I_{k}' \cdot J)(I_{k} \cdot J)] - (I_{k} \cdot J) J(J+1) \right\} \]

Concerning completeness compare footnote on page 2–383. In polyatomic molecules, \(AB\) corrections and pseudo-quadrupolar coupling are normally not considered. However, see for example [B87].

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Ref. p. 4-1] Magnetic constants: Polyatomic molecules 2–403

\[- \zeta (J_{K-1, K'}) \frac{1}{(2J + 3)(2J - 1)} [3(H \cdot J)^2 - H^2 J(J + 1)] = (2e)\]

\[- \sum_k \mu_n g^k_\| \sigma^k (J_{K-1, K'}) \frac{1}{(2J + 3)(2J - 1)} \left[ \frac{3}{2} (J^2 \cdot J)(H \cdot J) + (H \cdot J)(J^2 \cdot J) \right] - 2(J^2 \cdot H) J(J + 1) \]  
\[- \mu_n g^k_\| (1 - \sigma^k) J^2 \cdot H \]  
with \[C^k(J_{K-1, K'}) = \sum_k M_{kk}^k \frac{1}{J(J + 1)} \langle J_k^2 \rangle \, \]  
\[D_{kk}(J_{K-1, K'}) = 2 \sum_k M_{kk}^k \frac{1}{(J + 1)(2J + 3)} \langle J_k^2 \rangle \, \]  
\[g(J_{K-1, K'}) = \sum_k g_{kk} \frac{1}{J(J + 1)} \langle J_k^2 \rangle \, \]  
\[\xi (J_{K-1, K'}) = \sum_k (\zeta_{kk} - \zeta) \frac{1}{J(J + 1)} \langle J_k^2 \rangle \, \]  
\[\sigma^k(J_{K-1, K'}) = \sum_k (\sigma^k_{kk} - \sigma) \frac{1}{J(J + 1)} \langle J_k^2 \rangle \, \]  
\[\zeta = \frac{1}{3} \sum_k \zeta_{kk} \, \]  
\[\sigma^k = \frac{1}{3} \sum_k \sigma^k_{kk} \, \]  
\[\langle J_k^2 \rangle = \text{the expectation value of } J_k^2 \text{ over the state } J_{K-1, K'}. \]  
For nomenclature regarding rotational-energy states, see Table 2.5.

The scalar spin-spin coupling term is omitted since the electron-coupled spin-spin interaction seems to be beyond the resolution achievable with techniques reported here. \( \zeta \) as defined in (3f) is the bulk magnetic susceptibility, and \( \sigma^k \) as defined in (3g) is the average magnetic shielding at the \( k \)-th nucleus \( \zeta \) cannot be obtained spectroscopically since the term (2d) cancels out in subtracting energy levels.

Matrix element expressions depend on the coupling scheme which is adopted for nuclear spins \( P \) and rotational angular momentum \( J \), and are developed conveniently in terms of vector-coupling coefficients \([T10, H76]\).

The theoretical expressions for the molecular tensor quantities introduced above are as follows (principal-axis-of-inertia system throughout):

\[M_{kk}^k = M_{kk}^{par} + M_{kk}^{tor} = \frac{2|e| \mu_n g^k_\|| \xi_{kk} \xi_{kk} - (r_{kk})_{kk} (r_{kk})_{kk} \rangle \]  
\[+ \frac{2|e| \mu_n g^k_\| G_k}{hc \ m_{el}} \sum_{i,k} Z_i \langle r_{ki}^{-3} (r_{ki} \delta_{kk} - (r_{ki})_{kk} (r_{ki})_{kk}) \rangle \]  
\[+ \frac{2|e| \mu_n g^k_\| G_k}{hc \ m_{el}} \sum_{i,k} Z_i \langle r_{ki}^{-3} (r_{ki} \delta_{kk} - (r_{ki})_{kk} (r_{ki})_{kk}) \rangle \]  
\[+ \frac{2|e| \mu_n g^k_\| G_k}{hc \ m_{el}} \sum_{i,k} Z_i \langle r_{ki}^{-3} (r_{ki} \delta_{kk} - (r_{ki})_{kk} (r_{ki})_{kk}) \rangle \]  
\[D_{kk}^k = \frac{\mu_n g^k_\| G_k}{hc} \sum_{i,k} Z_i \langle r_{ki}^{-3} (r_{ki} \delta_{kk} - (r_{ki})_{kk} (r_{ki})_{kk}) \rangle [F7], \]  
\[g_{kk} = g^0_{kk} + g^1_{kk} = \frac{4\pi m_n G_k}{h} \sum_k Z_k \langle r_{kk} \delta_{kk} - (r_{kk})_{kk} (r_{kk})_{kk} \rangle \]  
\[+ \frac{4\pi m_n G_k}{h m_{el}} \sum_{n>0} (W_n - W_0)^{-1} \left( \langle 0 \mid L_k \mid n \rangle \langle n \mid L_k \mid 0 \rangle + \langle 0 \mid L_k \mid n \rangle \langle n \mid L_k \mid 0 \rangle \right) [E7], \]  
\[\zeta_{kk} = \zeta + \zeta_{par} = \frac{e^2 N}{4m_{el} c^2} \frac{\sum_i \langle r^2 \delta_{kk} - (r_{ki})_{kk} (r_{ki})_{kk} \rangle 0}{0} \]  
\[+ \frac{e^2 N}{2m^2 c^2} \sum_n (W_n - W_0)^{-1} \left( \langle 0 \mid L_k \mid n \rangle \langle n \mid L_k \mid 0 \rangle + \langle 0 \mid L_k \mid n \rangle \langle n \mid L_k \mid 0 \rangle \right) [V11], \]  
\[\sigma^k_{kk} = \sigma^k_{kk} + \sigma^k_{par} = \frac{e^2}{2m_{el} c^2} \frac{\sum_i \langle r^2 \delta_{kk} - (r_{ki})_{kk} (r_{ki})_{kk} \rangle} 0 \]  
\[- \frac{e^2}{2m^2 c^2} \sum_n (W_n - W_0)^{-1} \left( \langle 0 \mid L_k \mid n \rangle \langle n \mid L_k \mid 0 \rangle + \langle 0 \mid L_k \mid n \rangle \langle n \mid L_k \mid 0 \rangle \right) [R3], \]  
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where

- \( m_p \) = the proton mass
- \( h \) = Planck's constant divided by 2π
- \( c \) = the speed of light
- \( e \) = the electron charge
- \( m_e \) = the electron mass
- \( G_\ell \) = the rotational constant around axis \( \ell \)
- \( Z_k \) = the atomic number of the \( k \)-th nucleus
- \( \delta_{\ell k} \) = the Kronecker symbol
- \( r_{ik} = \sum_{\ell} \left( r_{ik}\right)^{\ell} \) = \( \rho \) = the distance between nucleus \( i \) and nucleus \( k \)

\( \left( r_{ik}\right)_\ell = \left( r_{i\ell} - r_{k\ell}\right) \) = the projection of \( r_{ik} \) on axis \( \ell \), \( r_{i\ell} \) being the \( \ell \)-th component of the position vector of the \( k \)-th nucleus measured from the center of mass

\( n_{ik}, \left(n_{ik}\right)_\ell \) = the corresponding quantities involving electron \( i \) and nucleus \( k \)

\( W_\ell - W_0 \) = the energy difference between \( \ell \)-th excited and electronic ground state

\( L_\ell = \sum_{i} \left( L_{ik}\right)_\ell \) = the \( \ell \)-th component of total electronic orbital angular momentum referred to the center of mass

\( \left(L_{ik}\right)_\ell = \sum_{i} \left(L_{ik}\right)_\ell \) = the \( \ell \)-th component of total electronic orbital angular momentum referred to nucleus \( k \)

\( \langle 0 | \ell \rangle \) = the matrix element connecting the electronic ground state and the \( \ell \)-th excited state.

Higher-order contributions to (4a)-(4e) have been omitted because the accuracy of the data presented is barely sufficient to resolve smaller terms. For instance, the nuclear diamagnetic contribution is not included in eq. (4d) though it can easily be taken into account from structural information if necessary.

The quantities (4a)-(4e) above are averages over the vibrational state in question. Vibrational ground-state data are normally handled in the rigid-rotor approximation. The error introduced thereby is considered to be less than 1% in the measured quantities. Thus, in computing \( M_{gh}^{ab} \) from structural information and observing that \( M_{gh}^{ab} \) and \( \sigma_{gh}^{ab} \) in eqs. (4a) and (4e) are the same but for a constant one obtains the diamagnetic and paramagnetic shielding, \( \sigma_{gh}^{ab} \) and \( \sigma_{gh}^{ac} \), from the measurement of \( M_{gh}^{ab} \) and \( M_{gh}^{ac} \). In a similar way, and far more used in practice, the diamagnetic and paramagnetic susceptibilities, \( \chi_{gh}^{ab} \) and \( \chi_{gh}^{ac} \), can be obtained from measurements of \( g_{gh}^{ab} \) and \( \xi_{gh}^{ac} \). However, the bulk susceptibility is needed in order to determine \( \xi_{gh}^{ac} \) (g = a, b, c) from the spectroscopically measured anisotropies (eqs. 2e), (3d)). Lacking gas-phase data, bulk susceptibilities measured in the liquid state are frequently used in order to obtain the desired information. The error introduced is normally not known.

The molecular electric quadrupole moments can be extracted from g-values and susceptibility anisotropies via [H77]

\[
\Theta_{\ell \ell'} = \frac{1}{8} \left| e \right|^2 \sum_{k} \left( (r_{ik})_{\ell}^2 - (r_{ik})_{\ell'}^2 \right) - \frac{1}{8} \left| e \right|^2 \sum_{i} \left( (r_{i\ell})_{\ell}^2 - (r_{i\ell})_{\ell'}^2 \right) |0\rangle
\]

\[
= - \frac{\hbar}{8 \pi m_p} \left| e \right|^2 \left( \frac{2 \epsilon_{aa} - \epsilon_{bb} - \epsilon_{cc}}{G_a - G_b - G_c} \right) - \frac{4 m_p c^2}{\left| e \right|^2} (2 \xi_{aa} - \xi_{bb} - \xi_{cc}).
\]

The expectation values

\[
\langle 0 | \sum_{k} ((r_{ik})_{\ell}^2 - (r_{ik})_{\ell'}^2) |0\rangle = \langle g^2 \rangle - \langle g_{\ell'}^2 \rangle, \quad g, g' = a, b, c \quad (6)
\]

follow directly from diamagnetic-susceptibility anisotropies, and the individual-coordinate values

\[
\langle 0 | \sum_{k} (r_{ik})_{\ell}^2 |0\rangle = \langle g_{\ell}^2 \rangle, \quad g = a, b, c \quad (6a)
\]

can be extracted if bulk susceptibility information is available.

2. Explanation of the columns in the tabulation

<table>
<thead>
<tr>
<th>Column</th>
<th>Parameters</th>
<th>Definitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>( g_{aa}, g_{bb}, g_{cc} )</td>
<td>molecular g-values induced by rotation around the principal axis ( g = a, b, \text{ or } c ). The corresponding magnetic moment is ( \mu_{g} = \mu_{0} g_{zz} \ell_{k} ) ( \mu_{g} ) the same quantity in linear and symmetric-top molecules referred to directions along and perpendicular to the molecular axis</td>
</tr>
<tr>
<td>Cont.</td>
<td>( g_{\parallel}, g_{\perp} )</td>
<td></td>
</tr>
<tr>
<td>Column</td>
<td>Parameters</td>
<td>Definitions</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>3 Cont.</td>
<td>( g(J_{K-1, K+1}) )</td>
<td>effective g-value of the rotational state ( J_{K-1, K+1} ); see eq. (3c)</td>
</tr>
<tr>
<td>4</td>
<td>( A_\xi_1 = 2 \xi_{aa} - \xi_{bb} - \xi_{cc} )</td>
<td>independent anisotropies of the magnetic susceptibility (per mole).</td>
</tr>
<tr>
<td></td>
<td>( A_\xi_2 = 2 \xi_{bb} - \xi_{cc} - \xi_{aa} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( A_\xi_3 = \xi_{cc} - \xi_{aa} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \xi(J_{K-1, K+1}) )</td>
<td>magnetic-susceptibility anisotropy (per mole) in symmetric-top and linear molecules</td>
</tr>
<tr>
<td></td>
<td>( \xi_{aa}, \xi_{bb}, \xi_{cc} )</td>
<td>effective magnetic-susceptibility anisotropy of the state ( J_{K-1, K+1} ), see eq. (3d)</td>
</tr>
<tr>
<td>5</td>
<td>( \Theta_{aa}, \Theta_{bb}, \Theta_{cc} )</td>
<td>paramagnetic susceptibilities (per mole), see eq. (4d)</td>
</tr>
<tr>
<td></td>
<td>( \Theta_{\parallel}, \Theta_{\perp} )</td>
<td>paramagnetic susceptibility (per mole), perpendicular to the molecular axis in linear and symmetric-top molecules</td>
</tr>
<tr>
<td></td>
<td>( \Omega_{aa}, \Omega_{bb}, \Omega_{cc} )</td>
<td>paramagnetic susceptibility (per mole), parallel to the molecular axis in symmetric-top molecules</td>
</tr>
<tr>
<td>6</td>
<td>( \Theta_{aa}, \Theta_{bb}, \Theta_{cc} )</td>
<td>molecular electric quadrupole moments, see eq. (5)</td>
</tr>
<tr>
<td></td>
<td>( \Theta_{\parallel}, \Theta_{\perp} )</td>
<td>molecular electric quadrupole moments in symmetric-top and linear molecules, see eq. (5)</td>
</tr>
<tr>
<td>7</td>
<td>( \langle a^2 \rangle, \langle b^2 \rangle, \langle c^2 \rangle ), or linear combinations thereof ( \langle |^2 \rangle, \langle \perp^2 \rangle ), or the difference of both</td>
<td>expectation values of the sums of the squares of the electronic center-of-mass coordinates, see eqs. (6), (6a)</td>
</tr>
<tr>
<td></td>
<td>( \langle |^2 \rangle, \langle \perp^2 \rangle )</td>
<td>the same quantities in linear and symmetric-top molecules referred to directions along and perpendicular to the molecular axis, see eqs. (6), (6a)</td>
</tr>
<tr>
<td>8</td>
<td>Meth.</td>
<td>experimental method yielding the values listed to the left or/and to the right of this column. Explanation of abbreviations see p. 2-402</td>
</tr>
<tr>
<td>9</td>
<td>Ref.</td>
<td>references for the values in columns 3...8 and for column 10</td>
</tr>
<tr>
<td>10</td>
<td>( g_{aa}, g_{bb}, g_{cc} )</td>
<td>nuclear contributions to the molecular g-values</td>
</tr>
<tr>
<td></td>
<td>( M_{aa}, M_{bb}, M_{cc} )</td>
<td>spin-rotation coupling tensor elements, see eq. (1a)</td>
</tr>
<tr>
<td></td>
<td>( M_{\parallel}, M_{\perp} )</td>
<td>spin-rotation coupling tensor elements of linear and symmetric-top molecules, nucleus ( k ) on the molecular axis, see eq. (1a)</td>
</tr>
<tr>
<td></td>
<td>( C^k(J_{K-1, K+1}) )</td>
<td>spin-rotation interaction strength of the rotational state ( J_{K-1, K+1} ), see eqs. (2a), (3a)</td>
</tr>
<tr>
<td></td>
<td>( g_k )</td>
<td>nuclear g-value; the corresponding nuclear magnetic moment is ( \mu_k^I = g_k \mu_B )</td>
</tr>
<tr>
<td></td>
<td>( D_{aa}, D_{bb}, D_{cc} )</td>
<td>spin-spin interaction tensor elements involving nuclei ( k ) and ( l ), see eq. (4b)</td>
</tr>
<tr>
<td></td>
<td>( D^{k\ell}(J_{K-1, K+1}) )</td>
<td>spin-spin interaction strength of the rotational state ( J_{K-1, K+1} ), see eq. (3b)</td>
</tr>
<tr>
<td></td>
<td>( \mu_2, \lambda, \mu_0, \mu_1, \mu_2, \lambda, \mu_0, \mu_1, \lambda )</td>
<td>spin-spin interaction parameters related to ( D_{aa} ) or ( D^{k\ell}(J_{K-1, K+1}) ) above, see eqs. (3b), (4b)</td>
</tr>
<tr>
<td></td>
<td>individual tensor components of the total and diamagnetic susceptibilities ( [10^{-6} \text{ erg/Gauss}^2 \text{ mole}] ), see eq. (4d)</td>
<td>the same quantities in linear and symmetric-top molecules referred to directions along and perpendicular to the molecular axis</td>
</tr>
<tr>
<td></td>
<td>bulk susceptibility ( [10^{-6} \text{ erg/Gauss}^2 \text{ mole}] ) used to obtain ( \xi_{aa}, \xi_{bb}, \xi_{cc}, \xi_{\parallel}, \xi_{\perp} )</td>
<td>the corresponding anisotropies ( \langle a^2 \rangle, \langle b^2 \rangle, \langle c^2 \rangle, \langle |^2 \rangle, \langle \perp^2 \rangle ) from the corresponding anisotropies</td>
</tr>
</tbody>
</table>

1) Different sign conventions are used in the literature for spin-rotation coupling constants. The signs have been converted to comply with the definition given in eqs. (1a), (2a), and (4a) if necessary. Thus, a positive value of \( M_{gg}^k \) indicates that the direction of the magnetic field at the site of the \( k \)-th nucleus as induced by molecular rotation around the \( g \)-th axis is determined by the electronic charge distribution (assuming a positive nuclear magnetic moment). |

2) The suffix \( k \) is sometimes left off if only one nucleus with \( I > 0 \) is present in the molecule. |

3) Spin-spin interaction parameters are given only if they are used in the spectral fit. In most cases authors obtain them from the known structure. |

4) Susceptibilities are given in units of \( 10^{-6} \text{ erg/Gauss}^2 \text{ mole} \) throughout. |

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### Parameters Definitions

<table>
<thead>
<tr>
<th>Column</th>
<th>Parameters</th>
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<tbody>
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<td>10 Cont.</td>
<td>$\sigma^k$</td>
<td>nuclear-magnetic shielding (ppm)</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{oa}, \sigma_{ab}, \sigma_{ar}$</td>
<td>nuclear-magnetic shielding tensor components (ppm)</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{\parallel}, \sigma_{\perp}$</td>
<td>nuclear-magnetic shielding tensor components (ppm) of linear and symmetric-top molecules, nucleus k on the molecular axis</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>references to tables 2.5 and 5.2</td>
</tr>
</tbody>
</table>

1) The suffix k is sometimes left off if only one nucleus with $I > 0$ is present in the molecule.

### 3. Arrangement of substances
a) Linear molecules

b) Symmetric top molecules:
- Pyramidal molecules, $XY_3$: 10–16
- Five-atom molecules, $XY_4$ and $XY_2Z$, $X=C, Si, Ge$: 17–29
- Other five atom molecules, $XYZ_3$: 30
- $CH_4$ derivatives of linear molecules: 31–34
- Symmetric two-top molecules: 34a
- Carbonyl compounds: 35, 36