

L.3.5 Spectroscopy

<i>Name</i>	<i>Symbol</i>	<i>Definition</i>	<i>SI unit</i>	<i>Notes</i>
total term	T	$T = E_{\text{tot}}/hc$	m^{-1}	(1), (2)
transition wavenumber	$\tilde{\nu}, (\nu)$	$\tilde{\nu} = T' - T''$	m^{-1}	(1)
transition frequency	ν	$\nu = (E' - E'')/h$	Hz	
electronic term	T_e	$T_e = E_e/hc$	m^{-1}	(1), (2)
vibrational term	G	$G = E_{\text{vib}}/hc$	m^{-1}	(1), (2)
rotational term	F	$F = E_{\text{rot}}/hc$	m^{-1}	(1), (2)
electric dipole moment of a molecule	$\mathbf{p}, \boldsymbol{\mu}$	$E_p = -\mathbf{p} \cdot \mathbf{E}$	C m	
transition dipole moment of a molecule	\mathbf{M}, \mathbf{R}	$\mathbf{M} = \int \psi'^* \mathbf{p} \psi'' d\tau$	C m	
interatomic distances,				
equilibrium	r_e		m	
zero-point average	r_z		m	
ground state	r_0		m	
substitution structure	r_s		m	

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- (1) In spectroscopy the unit cm^{-1} is almost always used for wavenumber, and term values and wavenumbers always refer to the reciprocal wavelength of the equivalent radiation in vacuum. The symbol c in the definition E/hc refers to the speed of light in vacuum.
- (2) Term values and rotational constants are sometimes defined in wavenumber units (e.g. $T = E/hc$), and sometimes in frequency units (e.g. $T = E/h$). When the symbol is otherwise the same, it is convenient to distinguish wavenumber quantities with a tilde (e.g., $\tilde{T}, \tilde{A}, \tilde{B}, \tilde{C}$ for quantities defined in wavenumber units), although this is not a universal practice.

Name	Symbol	Definition	SI unit	Notes
nuclear magnetic resonance (NMR):				
magnetogyric ratio	γ	$\gamma = \mu/Ih$	$\text{s}^{-1} \text{T}^{-1}$	
shielding constant	σ	$B_A = (1 - \sigma_A)B$	1	(3)
chemical shift, δ scale	δ	$\delta = 10^6(\nu - \nu_0)/\nu_0$	1	(4)
coupling constant, (indirect) spin-spin	J_{AB}	$\hat{H}/h = J_{AB} \hat{I} \cdot \hat{I}$	Hz	(5)
reduced spin-spin K_{AB}		$K_{AB} = \frac{J_{AB}}{h} \frac{2\pi}{\gamma_A} \frac{2\pi}{\gamma_B}$	$\text{T}^2 \text{J}^{-1}, \text{N A}^{-2}, \text{m}^{-3}$	(6)
direct (dipolar)	D_{AB}		Hz	(7)
relaxation time, longitudinal	T_1		s	(8)
transverse	T_2		s	(8)

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- (3) σ_A and B_A denote the shielding constant and the local magnetic field at nucleus A.
- (4) ν_0 is the resonance frequency of a reference molecule, usually tetramethylsilane for proton and for ^{13}C resonance spectra. In some of the older literature proton chemical shifts are expressed on the τ scale, where $\tau = 10 - \delta$, but this is no longer used.
- (5) \hat{H} in the definition is the spin-spin coupling hamiltonian between nuclei A and B.
- (6) Whereas J_{AB} involves the nuclear magnetogyric ratios, the reduced coupling constant K_{AB} represents only the electronic contribution and is thus approximately isotope independent and may exhibit chemical trends.
- (7) Direct dipolar coupling occurs in solids; the definition of the coupling constant is $D_{AB} = (\mu_0/4\pi)r_{AB}^{-3}\gamma_A\gamma_B(\hbar/2\pi)$.
- (8) The longitudinal relaxation time is associated with spin-lattice relaxation, and the transverse relaxation time with spin-spin relaxation. The definitions are
- $$dM_z/dt = -(M_z - M_{z,e})/T_1,$$
- and
- $$dM_x/dt = -M_x/T_2,$$
- where M_z and M_x are the components of magnetization parallel and perpendicular to the static field B , and $M_{z,e}$ is the equilibrium value of M_z .

<i>Name</i>	<i>Symbol</i>	<i>Definition</i>	<i>SI unit</i>	<i>Notes</i>
<i>electron spin resonance (ESR),</i>				
<i>electron paramagnetic resonance (EPR):</i>				
magnetogyric ratio	γ	$\gamma = \mu/sh$	$\text{s}^{-1} \text{T}^{-1}$	
g-factor	g	$h\nu = g\mu_B B$	1	
hyperfine coupling constant,				
in liquids	a, A	$\hat{H}_{\text{hfs}}/h = a \hat{\mathbf{S}} \cdot \hat{\mathbf{I}}$	Hz	(9)
in solids	\mathbf{T}	$\hat{H}_{\text{hfs}}/h = \hat{\mathbf{S}} \cdot \mathbf{T} \cdot \hat{\mathbf{I}}$	Hz	(9)

(9) \hat{H}_{hfs} is the hyperfine coupling hamiltonian. The coupling constants a are usually quoted in MHz, but they are sometimes quoted in magnetic induction units (G or T) obtained by dividing by the conversion factor $g\mu_B/h$, which has the SI unit Hz/T; $g_e\mu_B/h \approx 28.025 \text{ GHz T}^{-1}$ ($= 2.8025 \text{ MHz G}^{-1}$), where g_e is the g-factor for a free electron. If in liquids the hyperfine coupling is isotropic, the coupling constant is a scalar a . In solids the coupling is anisotropic, and the coupling constant is a 3×3 tensor \mathbf{T} . Similar comments apply to the g-factor.

Other symbols and conventions in optical spectroscopy

(i) Term symbols for atomic states

The electronic states of atoms are labeled by the value of the quantum number L for the state. The value of L is indicated by an upright capital letter: S, P, D, F, G, H, I and K, ..., are used for $L = 0, 1, 2, 3, 4, 5, 6$ and $7, \dots$, respectively. The corresponding lower case letters are used for the orbital angular momentum of a single electron. For a many-electron atom, the electron spin multiplicity $(2S + 1)$ may be indicated as a left-hand superscript to the letter, and the value of the total angular momentum J as a right-hand subscript. If either L or S is zero only one value of J is possible, and the subscript is then usually suppressed. Finally, the electron configuration of an atom is indicated by giving the occupation of each one-electron orbital as in the examples below.

Examples B: $(1s)^2(2s)^2(2p)^1, {}^2P_{1/2}$
 C: $(1s)^2(2s)^2(2p)^2, {}^3P_0$
 N: $(1s)^2(2s)^2(2p)^3, {}^4S$

(ii) Term symbols for molecular states

The electronic states of molecules are labelled by the symmetry species label of the wavefunction in the molecular point group. These should be Latin or Greek upright capital letters. As for atoms, the spin multiplicity $(2S + 1)$ may be indicated by a left superscript. For linear molecules the value of $\Omega (= \Lambda + \Sigma)$ may be added as a right subscript (analogous to J for atoms). If the value of Ω is not specified, the term symbols is taken to refer to all component states, and a right subscript r or i may be added to indicate that the components are regular (energy increases with Ω) or inverted (energy decreases with Ω) respectively.

The electronic states of molecules are also given empirical single letter labels as follows. The ground electronic state is labelled X, excited states of the same multiplicity are labelled A, B, C, ..., in ascending order of energy, and excited states of different multiplicity are labelled with lower case letters a, b, c, In polyatomic molecules (but not diatomic molecules) it is customary to add a tilde (e.g. \tilde{X}) to these empirical labels to prevent possible confusion with the symmetry species label.

Finally the one-electron orbitals are labelled by the corresponding lower case letters, and the electron configuration is indicated in a manner analogous to that for atoms.

Examples The ground state of CH is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^1, X {}^2\Pi_r$, in which the ${}^2\Pi_{1/2}$ component lies below the ${}^2\Pi_{3/2}$ component, as indicated by the subscript r for regular.

The ground state of OH is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^3, X {}^2\Pi_i$ in which the ${}^2\Pi_{3/2}$ component lies below ${}^2\Pi_{1/2}$ component, as indicated by the subscript i for inverted.