

# Energy level designations for diatomic molecules in VALD

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**Electronic states** of diatomic molecules are usually described in the following way:

$$label^{(2S+1)}|\Lambda|_{\Omega}$$

where  $S$ ,  $|\Lambda|$ , and  $\Omega$  are **quantum numbers (see below)**. Different **rotational-vibrational energy levels** within a state are described by additional **rotational quantum numbers** ( $J$ ,  $|\Sigma|$ ,  $N$ , see below) and the **vibrational quantum number**  $v$ . Furthermore, because the molecules are symmetric under certain symmetry operations, additional energy level splitting is introduced, which is described by **parity** labels.

The *label* is an uppercase or lowercase letter designating the electronic state.  $X$  is used for the ground state, and excited states of the same multiplicity ( $2S + 1$ ) as the ground state are labelled  $A, B, C, \dots$ , in order of increasing energy. Lowercase letters are used for states with a multiplicity different from that of the ground state. Sometimes, additional characters are appended to the letter.

Quantum numbers (see Bernath 2005, p. 324, Fig. 9.3):

- $S$  is the electron spin quantum number, corresponding to the total spin angular momentum  $\vec{S}$ .  $(2S + 1)$  is the **multiplicity** of the state.  
 $|\Sigma|$  is the quantum number associated with the magnitude of the projection of  $\vec{S}$  on the internuclear axis and assumes the values  $0, 1, \dots, S - 1, S$ .
- $\Lambda$  is the projection of total orbital angular momentum  $\vec{L}$  on the internuclear axis. In the state designation above,  $|\Lambda|$  is represented by capital greek characters:  $\Sigma, \Pi, \Delta, \Phi, \dots$  for  $|\Lambda| = 0, 1, 2, 3, \dots$ , respectively (note that the symbol  $\Sigma$  is used for two completely unrelated things, like  $S$  in atomic spectroscopy).  
The reflection symmetry operation  $\hat{\sigma}_v$  causes a twofold orbital degeneracy for each  $|\Lambda|$  value. For  $|\Lambda| > 0$ , each rovibrational level is split into two, designated by the **total parity** label (+ and -). This effect is called  $\Lambda$ -doubling. In the case of  $|\Lambda| = 0$ , there are two distinct  $\Sigma^+$  and  $\Sigma^-$  states, and the parity of the rotational levels is determined by the quantum numbers: For  $\Sigma^+$  states, the parity is + for even values of  $J - \Sigma$ , and - for odd  $J - \Sigma$ , for  $\Sigma^-$  the situation is reversed.  
In certain line lists, *e/f parity* is given instead of total parity. In that case, *e* parity designates those rotational levels with a total parity of  $+(-1)^J$  for integer  $J$  and  $+(-1)^{J-1/2}$  for half-integer  $J$ , whereas *f* parity designates those rotational levels with a total parity of  $-(-1)^J$  for integer  $J$  and  $-(-1)^{J-1/2}$  for half-integer  $J$ . For more details on parity see Bernath (2005), p. 348.
- $J$  is the rotational quantum number corresponding to total angular momentum (excluding nuclear spin)  $\vec{J} = \vec{L} + \vec{S} + \vec{R}$ , where  $\vec{R}$  is the angular momentum of nuclear rotation.

- $\Omega$  is the projection of  $\vec{J}$  on the internuclear axis. Since  $\vec{R}$  is perpendicular to the internuclear axis,  $\Omega = \Lambda + \Sigma$ . In practice, the label  $|\Omega| = |\Lambda + \Sigma|$  is used in the state designation, except when  $S > \Lambda$ , in which case  $\Omega = |\Lambda| + \Sigma$  is used.
- $N$  is the quantum number corresponding to the spin-free angular momentum  $\vec{N} = \vec{J} - \vec{S} = \vec{R} + \vec{L}$ .

For the description of rotational levels, **spin-orbit coupling** has to be taken into account (coupling of  $\vec{S}$  and  $\vec{L}$ ). There are several limiting cases for spin-orbit coupling, called *Hund's cases*, depending on the relative values of the spin-orbit coupling constant  $A$  and the rotational constant  $B$  (Brown and Carrington 2003, Ch. 6.7, p.224).

Here, we assume that for the states of molecular transitions considered for VALD, either Hund's case (a) –  $A|\Lambda| \gg BJ$  – or Hund's case (b) –  $A|\Lambda| \ll BJ$  – applies. In case (a),  $\vec{L}$  and  $\vec{S}$  are strongly coupled to the internuclear axis, and  $J, S, |\Lambda|, |\Sigma|, |\Omega|$  are good rotational quantum numbers. In case (b),  $\vec{S}$  is not coupled to the internuclear axis, and  $J, S, |\Lambda|, N$  are good rotational quantum numbers (Brown and Carrington 2003, Table 6.7, p. 226). Since  $|\Omega| = |\Lambda + \Sigma|$ , both cases are uniquely described by four rotational quantum numbers:  $J, S, |\Lambda|$ , and either  $|\Omega|$  or  $N$ .

As the applicability of the coupling cases depends on the molecular constants and the value of  $J$ , a single case might not be appropriate to describe all energy levels for a certain molecule. For example, for TiO, case (a) might apply to all levels for the triplet states except the highest  $J$ -levels of the B state ( $B$  is around  $0.5 \text{ cm}^{-1}$ , see e.g. Jørgensen et al. 1994, and  $A$  is about  $25 \text{ cm}^{-1}$  for the B state and  $50 \text{ cm}^{-1}$  for the others, according to Kotzian et al. 1989).

The **bottom line** is the following. To describe the energy levels of TiO and other heteronuclear diatomic molecules, the following information is included in VALD: the state label, the multiplicity  $2S + 1$ , the four quantum numbers  $J, |\Lambda|, |\Omega|$  or  $N$ , and  $v$ , and the total or  $e/f$  parity label. For homonuclear molecules, there is an additional symmetry (due to an inversion operation or nuclear permutation), which requires an additional parity label (electronic wavefunction inversion parity, value  $g$  or  $u$ , see e.g. Bernath 2005, p. 351). This parity is appended at the end of the term designation string if needed (see examples at end of this document).

**Quantum numbers adopted for TiO line lists:** The theoretical TiO line list provided by B. Plez for VALD includes the value of  $N$  (neither  $|\Omega|$  nor  $|\Sigma|$ ) for all energy levels. We therefore adopt Hund's case (b) for the level description for this line list. The theoretical TiO line list by Schwenke (1998) provided by R. Kurucz includes a quantum number with integer values between 1 and 5 for triplet states and between 1 and 3 for singlet states. We interpret this as a kind of  $|\Omega|$  for Hund's case (a).

Finally, following the format of the term designation field for atomic levels, we include the **dominant electronic configuration(s)** for valence electrons in the molecular level designation. In the configurations for molecular states, the electron orbitals are described by lowercase greek letters for the angular momentum quantum numbers of individual electrons. In the VALD record, we use the corresponding latin characters, so care should be taken not to confuse them with atomic orbitals.

The following table gives the dominant electronic configurations for the **TiO states** involved in the transitions included in VALD (Sennesal & Schamps 1987, Schwenke 1998, see also Barnes et al. 1997, Fig. 8):

State	Dominant configuration	Designation in VALD record
$X^3\Delta$	$8\sigma^2 9\sigma^1 3\pi^4 1\delta^1$	8s2.9s1.3p4.1d1
$A^3\Phi$	$8\sigma^2 3\pi^4 4\pi^1 1\delta^1$	8s2.3p4.4p1.1d1
$B^3\Pi$	$8\sigma^2 3\pi^4 4\pi^1 1\delta^1$	8s2.3p4.4p1.1d1
$C^3\Delta$	$8\sigma^2 11\sigma^1 3\pi^4 1\delta^1$	8s2.11s1.3p4.1d1
$D^3\Sigma^-$	$8\sigma^2 3\pi^4 1\delta^2$	8s2.3p4.1d2
$E^3\Pi$	$8\sigma^2 9\sigma^1 3\pi^4 4\pi^1$	8s2.9s1.3p4.4p1
$a^1\Delta$	$8\sigma^2 9\sigma^1 3\pi^4 1\delta^1$	8s2.9s1.3p4.1d1
$b^1\Pi$	$8\sigma^2 9\sigma^1 3\pi^4 4\pi^1$	8s2.9s1.3p4.4p1
$c^1\Phi$	$8\sigma^2 3\pi^4 4\pi^1 1\delta^1$	8s2.3p4.4p1.1d1
$d^1\Sigma^+$	$8\sigma^2 9\sigma^2 3\pi^4$	8s2.9s2.3p4
$f^1\Delta$	$8\sigma^2 11\sigma^1 3\pi^4 1\delta^1$	8s2.11s1.3p4.1d1
$g^1\Gamma$	$8\sigma^2 3\pi^4 1\delta^2$	8s2.3p4.1d2
$h^1\Sigma^+$	$8\sigma^2 3\pi^4 1\delta^2$	8s2.3p4.1d2

The next table gives the main electronic configurations for the **MgH states** involved in the transitions included in VALD (Guitou et al. 2010, Table 2). Multiple configurations for a level are separated by “/”.

State	Dominant configuration	Designation in VALD record
$X^2\Sigma^+$	$4\sigma^2 5\sigma^1$	4s2.5s1
$A^2\Pi$	$4\sigma^2 2\pi^1$	4s2.2p1
$B'^2\Sigma^+$	$4\sigma^1 5\sigma^2 / 4\sigma^2 7\sigma^1 / 4\sigma^2 6\sigma^1$	4s1.5s2/4s2.7s1/4s2.6s1

The table below gives the main electronic configurations for the **CH states** involved in the transitions included in VALD (Szalay and Nemes 1999).

State	Dominant configuration	Designation in VALD record
$X^2\Pi$	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^1$	1s2.2s2.3s2.1p1
$A^2\Delta$	$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$	1s2.2s2.3s1.1p2
$B^2\Sigma^-$	$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$	1s2.2s2.3s1.1p2
$C^2\Sigma^+$	$1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$	1s2.2s2.3s1.1p2

The following table gives the main electronic configurations for the **C<sub>2</sub> states** involved in the transitions included in VALD (Hirsch et al. 1980, Peterson 1995, Suter and Engels 1996, Bruna and Grein 2001). Multiple configurations for a level are separated by “/”. For an energy level diagram of all states see Tanabashi et al. (2007, Fig. 1).

State	Dominant configuration	Designation in VALD record
$X^1\Sigma_g^+$	$2\sigma_g^2 2\sigma_u^2 1\pi_u^4 / 2\sigma_g^2 3\sigma_g^2 1\pi_u^4$	2sg2.2su2.1pu4/2sg2.3sg2.1pu4
$A^1\Pi_u$	$2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_u^3$	2sg2.2su2.3sg1.1pu3
$a^3\Pi_u$	$2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_u^3$	2sg2.2su2.3sg1.1pu3
$b^3\Sigma_g^-$	$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2$	2sg2.2su2.3sg2.1pu2
$d^3\Pi_g$	$2\sigma_g^2 2\sigma_u^1 3\sigma_g^2 1\pi_u^3 / 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_g^1 1\pi_u^2$	2sg2.2su1.3sg2.1pu3/2sg2.2su2.3sg1.1pg1.1pu2
$e^3\Pi_g$	$2\sigma_g^2 2\sigma_u^1 3\sigma_g^2 1\pi_u^3 / 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_g^1 1\pi_u^2$	2sg2.2su1.3sg2.1pu3/2sg2.2su2.3sg1.1pg1.1pu2

In **summary**, molecular energy levels are characterized in the following way in a VALD record:

- energy  $E$  in  $\text{cm}^{-1}$  and rotational quantum number  $J$  in their respective fields,
- coupling case in the 2-character “coupling type” field,
- electronic configuration, state label, multiplicity, three quantum numbers, and parity label(s) in the 86-character “term designation” field.

For the coupling cases, the current options are “Ha” and “Hb” for Hund’s cases (a) and (b), respectively.

The **format** of the “term designation” field is the following: The electronic configuration according to the table above (a string of characters without spaces) is followed by one or more spaces, followed by a comma-separated string containing, in that order, *label*, *multiplicity*,  $|\Lambda|$ , *parity*,  $|\Omega|$  or  $N$ ,  $v$ .

- *label* is an upper- or lowercase latin character
- *multiplicity* is a non-negative integer number
- $|\Lambda|$  is a non-negative integer number
- *parity* is a +, -, 0, e, or f character. 0 is a special case related to  $\Lambda$ -doubling: it means that the transition is double-degenerate, but the two lines have the same wavelength ( $\Lambda$ -doubling is not resolved), and have been merged into one line by multiplying the  $gf$ -value by 2.
- $|\Omega|$  (Hund a) and  $N$  (Hund b) are real numbers (non-negative integers or half-integers)
- $v$  is a non-negative integer number
- electronic wavefunction inversion parity is a g or u character (if applicable).

### Examples:

Molecule	El. state	$E$ [ $\text{cm}^{-1}$ ]	$J$	Coupling	El. configuration, label and numbers
$^{48}\text{TiO}$	$X^3\Delta$	0.0000	1.0	Hb	8s2.9s1.3p4.1d1 X,3,2,-,0.0,0
$^{48}\text{TiO}$	$X^3\Delta$	4917.5441	4.0	Hb	8s2.9s1.3p4.1d1 X,3,2,+,3.0,5
$^{48}\text{TiO}$	$B^3\Pi$	30985.7588	104.0	Hb	8s2.3p4.4p1.1d1 B,3,1,-,104.0,12
$^{48}\text{TiO}$	$d^1\Sigma^+$	28893.8426	198.0	Hb	8s2.9s2.3p4 d,1,0,+,198.0,3
$^{48}\text{TiO}$	$C^3\Delta$	31175.5818	10.0	Hb	8s2.11s1.3p4.1d1 C,3,2,0,11.0,15
$\text{C}_2$	$a^3\Pi_u$	3262.790	9.0	Hb	2sg2.2su2.3sg1.1pu3 a,3,1,e,8.0,1,u

The last TiO row is an example for a merged line (total parity = 0). The  $\text{C}_2$  row shows an example with  $e/f$  parity and “electronic wavefunction inversion parity” ( $g/u$ ).

## References

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