Molecular Term Symbols

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Molecular term symbols specify molecular electronic energy levels. Term symbols for diatomic molecules are based on irreducible representations in linear symmetry groups, derived fromspectroscopic notations. They usually consist of four parts: spin multiplicity, azimuthal angular momentum, total angular momentum and symmetry. All molecular term symbols discussed here are based on Russel-Saunders coupling.

Introduction

Molecular term symbols mark different electronic energy levels of a diatomic molecule. These symbols are similar to atomic term symbols, since both follow the Russell-Saunders coupling scheme. Molecular term symbols employ symmetry labels from group theory. The possibility of an electronic trasition can be deducted from molecular term symbols following selection rules. For multi-atomic molecules, symmetry labels play most of term symbols' roles.

Group theory and symmetry for molecules

Molecules have certain symmetries, which can be described using point groups[1]. Here are the most common symmetry groups for molecules:

- Non-axial groups C_1, C_s, and C_i. The second has a mirror plane while the third has an center of inversion.
- Cyclic groups: C_n, where n is 1,2,3,4,5,6... They have an n-fold proper axis of rotation.
- Cyclic groups with a vertical mirror plane: C_{nv}.
- Cyclic groups with a horizontal mirror plane: C_{nh}.
- Dihedral groups: D_n. They have n evenly angled 2-fold proper axes of rotation perpendicular to an n-fold one.
- Dihedral groups with a dihedral mirror plane: D_{nd}.
- Dihedral groups with a horizontal mirror plane: D_{nh}.
- Spiral groups: S_n. They have one n-fold improper axis of rotation, when n is an even number.

- Linear groups: $C_{\infty v}$ and $D_{\infty h}$. These two are still a C_{nv} or a D_{nh} group, yet $n = \infty$ instead of a finite number.
- Tetrahedral groups: T_d and T_h. Their major axes are four 3-fold proper rotational axes. T_d has six dihedral mirrors while T_h has not only σ_d's but also horizontal mirrors to the major axes.
- Octahedral group: O_h. It has the same symmetry as a cube or an octahedron.
- Icosahedral group: I_h. It has the same symmetry as a dodecahedral or an icosahedron.
- Spheric group: K. It's theoretically the highest symmetric 3-dimensional point group.

  The properties or parts of a molecule may transform differently from the molecule itself under certain operations, even if the molecule is symmetric with respect to these operations. Character tables describe how objects transform under all operations of a symmetry group. Each object may have one particular set of characters. A set of characters for an object is called a representation. A representation is irreducible if it cannot be reduced into the sum of other representations. Different symmetry groups have different irreducible representations, yet some symmetry groups may share irreducible representations, which can either be the same or be totally different. For a detailed discussion into group theory, please refer to Group Theory: Theory and its application to chemistry.

Molecular Orbital Theory

Molecular orbital theory is a set of concepts and methods that allows us to understand the nature of molecules with respect to symmetry and energy. The theory assumes that all atomic orbitals within a molecule combine and form molecular orbitals, in which electrons are totally delocalized. These combinations should be formed by energetically and symmetrically "close-to-each-other" atomic orbitals. Molecular orbitals have certain symmetries according to the point group of the molecule. These symmetries can be represented by irreducible representations. Usually an MO diagram can be drawn for a molecule to depict its orbitals in terms of symmetry, energy and also electronic configuration.

Diatomic molecules

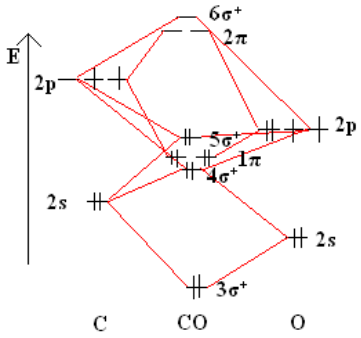
A diatomic molecule, or a diatomic, is formed by two same or different atoms bound by either covalent bonds or ionic bonds. It is homonuclear if the two atoms are the same, or heteronuclear if different.

Symmetries of diatomic molecules

In group theory, heteronuclear diatomic molecules have $C_{\infty v}$ symmetries, and homonuclear ones have $D_{\infty h}$ symmetries. There are infinitely many representations in both groups, among which the irreducible representations are symbolized using the notations "Σ, Π, Δ, etc." Both kinds of groups bear a perpendicular mirrow plane, or σ_v. So "+" and "-" are used to categorize the symmetry with respect to σ_v. $D_{\infty h}$symmetries indicate an inversion center in the molecule, yet $C_{\infty v}$ symmetries do not. For $D_{\infty h}$, irreducible representations are further classified by parity, using the "g" and "u" symbols.

MO diagrams for diatomic molecules

MO diagrams describe the electronic interaction within a molecule using linear combinations of the atomic orbitals. The orbitals are filled with electrons in an energetical order.



For example, the CO molecule is heteronuclear, which has a $C_{\infty v}$ symmetry. As shown in the diagram above, molecular orbitals are labeled with the irreducible representations they belong to. Note there is hybridization among the molecular orbitals of CO, so the ordering in energy levels is different from the MO diagrams of O_2 and F_2.

Term symbols of diatomic molecules

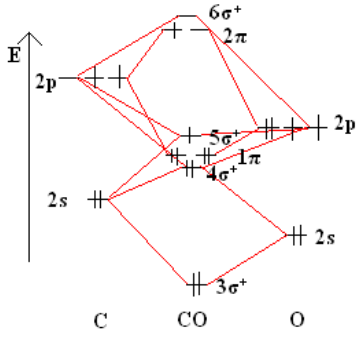
As mentioned above, the symmetries and parities are different between a heteronuclear diatomic and a homonuclear one. Their term symbols usually have different formats. For homonuclear diatomics, the term symbol has the following form:

$$2S+1\Lambda(+/-)\Omega,(g/u)$$

whereas Λ is the projection of the orbital angular momentum along the internuclear axis: Ω is the projection of the total angular momentum along the internuclear axis; *g*/*u* is the parity; and +/− is the reflection symmetry along an arbitrary plane containing the internuclear axis. Λ may be one of the greek letters in the sequence: Σ Π Δ Φ... when Λ = 0, 1, 2, 3..., respectively. For heteronuclear diatomics, the term symbol does not include the *g*/*u* part, for there is not inversion center in the molecule.

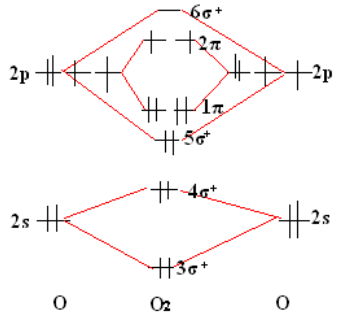
Determining term symbols of diatomics

Let's start with CO again. As we have seen before, the molecule has a close-shell configuration. Its ground state is a totally symmetric singlet, $^1\Sigma^+$, since the only possible values of (*S*, Λ) are (0, 0). If one of the HOMO electrons on the $5\sigma^+$ orbital has jumped to the LUMO, this molecule will be in an excited state as follows.



Suppose a CO molecule is in the excited state shown above. In order to know the term symbol of this state, a direct product of the labels is required for the two MO's with unpaired electrons. The multiplication is such as $\Pi \times \Sigma^+ = \Pi$. According to Pauli's exclusion rule, these two unpaired electrons can never share the same set of quantum numbers, therefore the spin degeneracy *S* can reach its maximum 3. The resulting term symbols are $^1\Pi$ and $^3\Pi$.

Now if we look at O_2, it does not have a close-shell configuration at its ground state. There are two unpaired electrons each occupying one of the two degenerate 2π orbitals, which can be seen in the diagram below.



The term symbol for oxygen molecule at its ground state is therefore derived such as $\Pi \times \Pi = \Sigma^+ + \Sigma^- + [\Delta]$, as the symbol in brackets does not allow the oxygen atoms to commute.

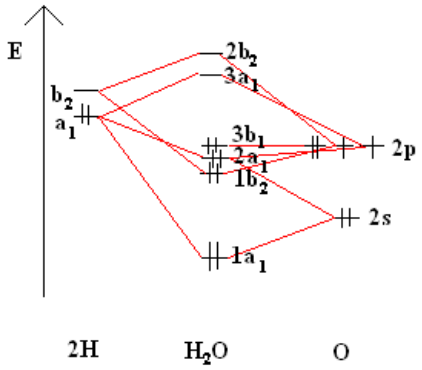
Transition between electronic states of diatomics

We'll focus on selection rules. Like atomic electronic states, different selection rules apply when differently incurred transitions occur. Usually for electric dipole field induced transitions, the selection rules are the same as for atoms.

1. $\Delta\Lambda = 0, \pm 1$ except $\Lambda = 0 \ddagger \Lambda' = 0$
2. $\Delta S = 0$
3. $\Delta\Omega = 0; \pm 1$ except $\Omega = 0 \ddagger \Omega' = 0$

Multi-atomic molecules

Multi-atomic molecules can either be linear or not, so the notations of them may look similar to that of a diatomic molecule or not. Irreducible representations of the symmetry groups are commonly used to mark the electronic states, which to some extent serve as term symbols. The direct product method still applies to multi-atomics.



As you can see in the MO diagram for H_2O above, each hydrogen atom provides a 1s orbital and they combine and form an A_1 orbital and a B_2 orbital before mixing with the atomic orbitals of oxygen. The A_1 and the B_2 orbitals are the SALC's, or the symmetry-allowed linear cominations of the hydrogen 1s orbitals. The SALC's symmetry labels can be determined by inspection. These SALC's may form molecular orbitals with corresponding atomic orbitals of oxygen.

In representing transitions, spectral notations including symmetry labels and spin complexity are used in multi-atomic molecules, instead of angular moment. These notations like $^3A_1$ usually play similar roles as term symbols. Please refer to Selection Rules for detailed discussions on it.

References

1. Harris, Daniel C. (republished in 1989). Dover Publications. pp. 421-478. ISBN 0-486-66144-X
2. D. J. Willock (2009). *Molecular Symmetry*. John Wiley & Sons Ltd. ISBN 0-470-85348-4

Outside Links

- http://en.wikipedia.org/wiki/Molecular_term_symbol

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