Spectroscopy

**edited by
B. P. Straughan
and S. Walker**

**Electronic, Fluorescence,
Phosphorescence, and
Photoelectron Spectroscopy,
Quantum Numbers,
Dissociation Energies,
and Astrochemistry**

Spectroscopy
VOLUME THREE

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Preface

It is fifteen years since Walker and Straw wrote the first edition of 'Spectroscopy' and considerable developments have taken place during that time in all fields of this expanding subject. In atomic spectroscopy, for example, where the principles required in a student text have been laid down for many years, there have been advances in optical pumping and double resonance which cannot be neglected at undergraduate level. In addition, nuclear quadrupole resonance (n.q.r.) and far infrared spectroscopy now merit separate chapters while addtional chapters dealing with Mössbauer spectroscopy, photoelectron spectroscopy and group theory are an essential requisite for any modern spectroscopy textbook.

When the idea for a new edition of Spectroscopy was first discussed it quickly became clear that the task of revision would be an impossible one for two authors working alone. Consequently it was decided that the new edition be planned and co-ordinated by two editors who were to invite specialists, each of whom had experience of presenting their subject at an undergraduate level, to contribute a new chapter or to revise extensively an existing chapter. In this manner a proper perspective of each topic has been provided without any sacrifice of the essential character and unity of the first edition.

The expansion of subject matter has necessitated the division of the complete work into three self contained volumes.

Volume 1 includes atomic, n.m.r., n.q.r., e.s.r. and Mössbauer spectroscopy.

Volume 2 contains chapters on molecular symmetry and group theory, microwave, infrared and Raman, far-infrared spectroscopy, force constants, evaluation of thermodynamic functions.

Volume 3 centres on the information which results when a valence electron(s) is excited or removed from the parent molecule. It includes electronic spectroscopy, quantum numbers, dissociation energies, fluorescence and phosphorescence spectroscopy, astrochemistry, photoelectron spectroscopy.

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The complete work now provides a single source of reference for all the spectroscopy that a student of chemistry will normally encounter as an undergraduate. Furthermore the depth of coverage should ensure the books' use on graduate courses and for those starting research work in one of the main branches of spectroscopy.

A continued source of confusion in the spectroscopic literature is the duplication of symbols and the use of the same symbol by different authors to represent different factors. The literature use of both SI and non SI units further complicates the picture. In this book we have tried to use SI units throughout or units such as the electron volt which are recognised for continued use in conjunction with SI units. The symbols and recognised values of physical constants are those published by the Symbols Committee of the Royal Society 1975.

Acknowledgements

Contents

1 Molecular quantum numbers of diatomic molecules

1.1 FORMATION OF MOLECULAR QUANTUM NUMBERS

In the study of atomic spectra it was necessary to introduce the principal quantum number (n), the azimuthal quantum number (l), the electron and nuclear spin quantum numbers (s and I, respectively) or some combination of these. In addition, to account for the behaviour of the spectral lines of atoms in the presence of various electric or magnetic fields further quantum numbers were required.

When two atoms combine to give a diatomic molecule, these quantum numbers may be related to a new set of quantum numbers which characterize the electronic energy states of the molecule. In some respects diatomic molecules behave like atoms (see Vol. 1), and their energy distribution seems to follow a reasonably similar type of pattern. This is strikingly illustrated by comparing the electron states of the molecules with those of the atoms containing the same number of electrons. This comparison may be observed in Fig. 1.1. The main way in which they differ results from the presence of two nuclei; these produce a cylindrically symmetrical force field about the internuclear axis.

In an atom $l_1, l_2, l_3, \ldots$ couple together to give L, while $s_1, s_2, s_3, \ldots$ give a resultant electron spin quantum number S. The resultant orbit angular momentum is then $\sqrt{[L(L + 1)]} h/2\pi$, and the resultant electron spin angular momentum $\sqrt{[S(S + 1)]} h/2\pi$. When an atom characterized by $\sqrt{[L_1(L_1 + 1)]} h/2\pi$ and $\sqrt{[S_1(S_1 + 1)]} h/2\pi$ combines with another characterized by $\sqrt{[L_2(L_2 + 1)]} h/2\pi$ and $\sqrt{[S_2(S_2 + 1)]} h/2\pi$ the possible values of L and S for the molecule are given by:

$$L = L_1 + L_2, L_1 + L_2 - 1, \ldots, |L_1 - L_2| \qquad (1.1)$$

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$$S = S_1 + S_2, S_1 + S_2 - 1, \ldots, |S_1 - S_2| \qquad (1.2)$$

An atom, however, unlike a diatomic molecule, has a spherically symmetrical force field. In a diatomic molecule, there is a strong electric field along the internuclear axis due to the electrostatic field of the two nuclei. The result is that the orbit and spin orbit angular momenta are uncoupled in this cylindrically symmetrical force field. The effect is that the corresponding $L^* h/2\pi$ and $S^* h/2\pi$ vectors for the resultant orbit and total spin angular momentum, respectively,[†]
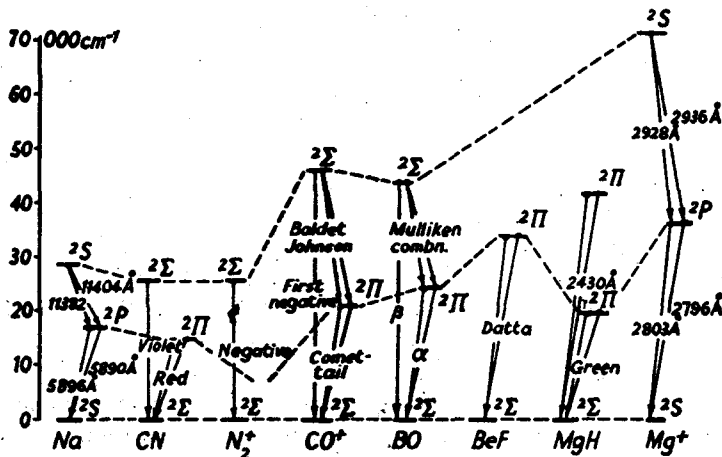
Fig. 1.1 Electronic energy levels of 13-electron molecules compared with those of Na and Mg$^+$ [1.2]. Corresponding levels are connected by broken lines, and observed lines and band systems are indicated by arrows. The names used to characterize some of the electronic transitions are also given. (Courtesy of Dr. W. Jevons, and the Council of the Physical Society, London)

precess independently about the internuclear axis,[‡] and $L^* h/2\pi$ has a constant component in that direction of $M_L h/2\pi$ where $M_L = L, L - 1, \ldots, -L$. In an electric field, if the direction of motion of all the electrons is reversed, the energy of the molecule remains unchanged, although the positive M_L value is changed into a negative one. It follows, therefore, that only states with different M_L values possess different energies. These different energy states are characterized by a quantum number Λ which defines the constant component of the resultant orbital angular momentum $(\sqrt{[L(L + 1)]} h/2\pi)$ for each energy state

[†] The shorthand representation of the form $X^* h/2\pi$ will be used for $\sqrt{[X(X + 1)]} h/2\pi$, where X may be L, S, J or K.

[‡] Whether $L^* h/2\pi$ and $S^* h/2\pi$ are uncoupled depends on the strength of the internal electric field. The latter is dependent on the internuclear distance, and when this is relatively large, then the electric field becomes too weak to uncouple $L^* h/2\pi$ and $S^* h/2\pi$, and they form a common resultant vector. This is dealt with later under Hund's case (c). The treatment given here for the uncoupling of $L^* h/2\pi$ and $S^* h/2\pi$ corresponds to Hund's case (a).

along the internuclear axis where Λ may take the values $0, 1, 2, 3, \ldots, L$.[†] The precession of the resultant orbit angular momentum about the internuclear axis is illustrated in Fig. 1.2(a).

The actual value of Λ is a measure of the number of units of angular momentum (in $h/2\pi$ units) resulting from projecting the electron orbit angular momentum along the internuclear axis. This component, $\Lambda h/2\pi$, along the axis always remains defined, whereas $L^* h/2\pi$ itself frequently is not.
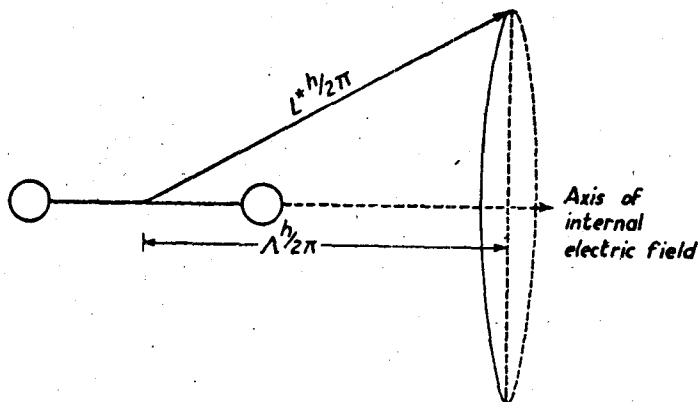
(a)
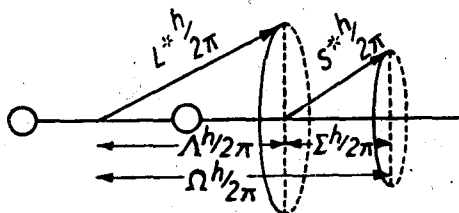
(b)

Fig. 1.2 (a) Precession of the resultant orbital angular momentum about the internuclear axis of a diatomic molecule. (b) Vector model for the precession of $L^* h/2\pi$ and $S^* h/2\pi$ in a diatomic molecule.

The electronic states of diatomic molecules are characterized by:

$$\Lambda = 0, 1, 2,$$

and are called a Σ-state, Π-state, and Δ-state, respectively. This is a parallel

[†] This type of classification applies not only to diatomic molecules but to linear polyatomic molecules as well. In both cases the electric field is cylindrically symmetrical about the axis through the nuclei. For more complex molecules the electronic states are classified on the basis of symmetry properties in terms of group theory.

classification to that employed for atoms, where when:

$$L = 0, 1, 2$$

these are termed S-, P-, and D-states, respectively.

The effect of electron spin cannot be neglected when attempting to define a molecular electronic state by means of quantum numbers; the total electron spin quantum number S must be taken into account. Each electron has a spin of $\pm\frac{1}{2}$ from which the resultant spin of the individual atoms may be evaluated. If S_1 and S_2 are the resultant spins in the separate atoms, then the possible values for the resultant electronic spin, S, of the molecule are given by:

$$S = S_1 + S_2, S_1 + S_2 - 1, \ldots, |S_1 - S_2| \qquad (1.3)$$

The value of S may be integral or half-integral, depending on whether the total number of electrons is even or odd. If the component of the electron orbit angular momentum ($L^* h/2\pi$) along the internuclear axis is not zero, that is, it is not a Σ-state, then there exists an internal magnetic field† (acting along the internuclear axis). The field is produced by the orbital motion of the electrons and may be identified with the precession of the orbit angular momentum. The magnetic moment associated with the electron spin can interact with this internal magnetic field causing a precession of the spin angular momentum about the internuclear axis. The component values of this spin angular momentum along this axis are governed by another quantum number Σ ‡ which takes the values:

$$\Sigma = S, S - 1, S - 2, \ldots, -S \qquad (1.4)$$

Thus, Σ is analogous to the symbol M_S employed in the case of atoms, and $\Sigma h/2\pi$ is the value of the spin orbit angular momentum about the internuclear axis, there being $(2S + 1)$ possible orientations. The vector model for the precession of $L^* h/2\pi$ and $S^* h/2\pi$ is given in Fig. 1.2(b).

The component of the total electron angular momentum along the internuclear axis may be obtained by coupling Λ and Σ:

$$|\Lambda + \Sigma| = \Omega \qquad (1.5)$$

where $\Omega h/2\pi$ is the total electron angular momentum about the internuclear

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† The magnetic moment of the spinning electron cannot interact directly with the internuclear electric field as does the induced electric dipole moment associated with the resultant orbit angular momentum vector. The latter is governed by the torque exerted by the electric field which causes it to precess about the internuclear axis and to have quantized components along this axis.
‡ This is the sloping Greek capital Σ, and it is necessary not to mistake this for the upright symbol Σ which is used to represent a molecular state $\Lambda = 0$.

axis.† The combination of Λ and Σ in this way to give Ω is to be compared with the corresponding case of atoms in a strong electric field, where $|M_L| + M_S = M_J$. For each value of Λ there are $(2S + 1)$ sublevels determined by the $(2S + 1)$ values of Σ, and the multiplicity is, thus, $(2S + 1)$; this value is added as a left superscript to the electronic state symbol. For example, a state for which Λ is equal to 1 having a spin of 1 would be the $^3\Pi$-state. The value of Ω is indicated as a right subscript to the main symbol; in this case $\Sigma = 1, 0$, and -1, and $\Omega = 1 + \Sigma$ and has $2 \times 1 + 1$ values which are 2, 1, and 0. The three different electronic energy states for the molecule in this quantum condition would thus be $^3\Pi_2$, $^3\Pi_1$, and $^3\Pi_0$, and would be represented by three different potential energy curves.

The splitting of the energy levels in a multiplet state may be related to the values of the quantum numbers Λ and Σ. For example, the electronic energy of term value T_e of a multiplet term is given approximately by:

$$T_e = T_0 + A\Lambda\Sigma$$

where T_0 is the term value when $\Sigma = 0$. A is known as the *coupling constant* and fixes the magnitude of the multiplet splitting; its value increases rapidly with the size of the atoms as does the multiplet splitting $(T_e - T_0)$.
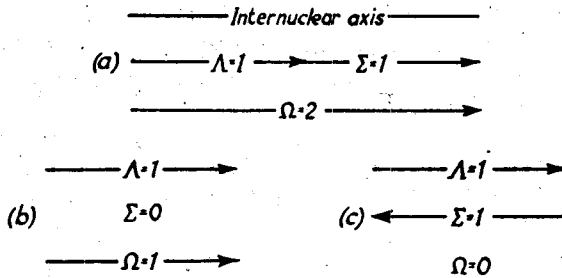
Fig. 1.3 Vector diagram of (a) $^3\Pi_2$, (b) $^3\Pi_1$, and (c) $^3\Pi_0$ states.

The relative orientations of the vectors Λ and Σ in the $^3\Pi_2$, $^3\Pi_1$, and $^3\Pi_0$ states are illustrated in Fig. 1.3, and neglecting all considerations of rotational and vibrational levels the corresponding three electronic states may be represented as in Fig. 1.4.

The coupling constant A is constant for a given multiplet term. A coupling constant may have a positive or negative value, and in the case in Fig. 1.4, if A

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† This is really Hund's case (a) (see later). In case (b) the angular momentum along the internuclear axis is $\Lambda h/2\pi(= \Omega h/2\pi)$ while in case (c) $L^* h/2\pi$ and $S^* h/2\pi$ remain coupled, and it is the presence of their resultant vector which gives the value of $\Omega h/2\pi$. Thus, for cases (a), (b), and (c) of Hund's coupling the angular momentum along the internuclear axis in each case may be regarded as being $\Omega h/2\pi$.

Fig. 1.4 Energy level diagram of a $^3\Pi$-state.

had been negative, then the $^3\Pi_2$ level would interchange places with the $^3\Pi_0$ level.

When $\Lambda = 0$, this means that the component of the resultant electron orbit angular momentum along the internuclear axis is zero; hence, the magnetic field along this line will also be zero and no splitting of the energy levels will occur. For example, if $\Lambda = 0$ and $S = 2$ this would be represent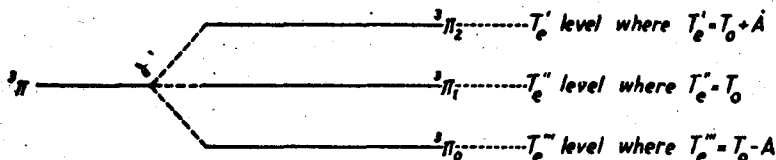ed by a $^5\Sigma$-state, but there would be no splitting of this electronic energy state. This is in harmony with putting $\Lambda = 0$ in the formula $T_e = T_0 + A\Lambda\Sigma$, whence $T_e = T_0$. Thus, superficially the superscript symbol may seem somewhat misleading. However, even for Σ-states a small amount of splitting of the electron states may occur when $(2S + 1) > 1$ provided that the molecule is rotating. This type of splitting results from interaction of the magnetic moment due to electron spin with the magnetic field due to molecular rotation.[†] As regards molecules in other than Σ-states (e.g. Π and Δ) the full splitting of the electronic energy levels required by $(2S + 1)$ generally seems to occur.

1.2 'SCRIPTS' GIVING INFORMATION ON THE WAVEFUNCTION SYMMETRY OF DIATOMIC MOLECULES

Another superscript is used in addition to the one denoting multiplicity and this is a right-hand one with $+$ or $-$ sign. These signs give information on the symmetry characteristics of the wavefunction of a molecular electronic state. If the wavefunction of the electron eigenfunction does not change sign on reflection of the coordinates to the other side of a plane between the two nuclei, then the $+$ superscript is given, and if the sign is changed, the electronic state is characterized by a $-$ superscript.

A right-hand subscript of g or u attached to the electronic energy state symbol is also employed. This is used when the atoms joined by the bond are identical or are isotopes of the same element. Such a system has a centre of symmetry.

If the coordinates of all the electrons x_i, y_i, z_i are replaced by $-x_i, -y_i$, and $-z_i$, then provided that the electron eigenfunction remains unaltered in sign by

† This magnetic field is produced by the rotation of the nuclei as a pair about a common centre of gravity, and consequently a perpendicular magnetic field is produced in the direction of the vector representing the nuclear angular momentum.

this reflection through the centre of symmetry, the subscript g is attached. If the sign of the wavefunction changes, a subscript u is employed. The g symbol is derived from the German *gerade* denoting even and u from *ungerade* meaning odd. Thus, a molecule characterized by the symbol g is regarded as having an even state indicating that on reflection of the electron eigenfunction at the centre of symmetry its sign is unchanged and conversely so for the u symbol.
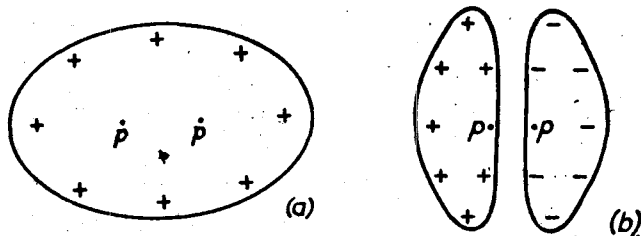

Fig. 1.5 (a) A bonding orbital, e.g. a $^2\Sigma_g^+$-state. (b) An antibonding orbital, e.g. a $^2\Sigma_u^+$-state.

As an example of the use of + and − symmetry and g and u, the molecular orbit of the H_2^+ will now be considered. The bonding orbit is shown in Fig. 1.5(a) and the non-bonding orbit in Fig. 1.5(b). The positive and negative signs inside the boundary indicate that the wavefunction ψ is positive and negative, respectively, in that region, while the p represents a proton. If a plane is placed through the two protons, then on either side of the plane the wavefunction does not change sign on reflection through the plane; hence, a + sign is attached as a superscript to the term symbol. If a straight line is drawn between the centres of the two protons, then the mid-point would be the centre of symmetry, and if this is made the origin of the coordinates (x, y, z) it follows from Fig. 1.5(a) that on replacement of these coordinates by $(-x, -y, -z)$ the wavefunction will still be positive; hence, the symbol g is used for this case. In Fig. 1.5(b), however, by a similar procedure the wavefunction would be negative; hence, for this case, the symbol u would be employed. As there is only one electron, the multiplicity must be $2 \times \frac{1}{2} + 1 = 2$, and this is added as the left-hand superscript; hence, the bonding orbital is described by $^2\Sigma_g^+$ but the antibonding orbital by $^2\Sigma_u^+$.

1.3 CORRELATION BETWEEN ATOMIC AND MOLECULAR STATES

A further link between atomic and molecular spectra is that various rules have been evolved as to which possible molecular electronic states may result from the combination of two atoms in known electronic states to form a diatomic molecule. These rules emerge from quantum mechanics where only certain multiplicities and molecular states are permissible from the combination of any

two atomic states. For instance a few of the examples on how atomic and molecular multiplicities may be related are given in Table 1.1.

Table 1.1 Feasible molecular multiplicities resulting from
the combination of two atoms of known multiplicity

Atomic multiplicity	Resulting molecular multiplicity
singlet + singlet	singlet
singlet + doublet	doublet
doublet + doublet	singlet or triplet
triplet + triplet	singlet or triplet or quintet

In Table 1.2 the molecular electronic states which may result from combining two atomic states of known multiplicity to form a symmetrical diatomic molecule are given. Once, however, P- and D-states are considered, the number of feasible resulting molecular states considerably increases.

Table 1.2 Feasible molecular states of a symmetrical diatomic molecule resulting from the combination of known atomic states

Atomic states	Resulting molecular state
$^1S + {}^1S$	$^1\Sigma_g^+$
$^2S + {}^2S$	$^1\Sigma_g^+$ or $^3\Sigma_u^+$
$^3S + {}^3S$	$^1\Sigma_g^+$ or $^3\Sigma_u^+$, or $^5\Sigma_g^+$

For example, the combination of two atoms in a ^{1}P-state may result in $^1\Sigma_g^+$, $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^1\Delta_g$ states, while ^{1}D + ^{1}D may give nine different molecular states.

1.4   COUPLING OF ANGULAR MOMENTA

1.4.1   Introduction

So far we have considered the rotation of a diatomic molecule with respect to the rotation of the nuclei only. However, this rotation and the rotational energy equation may be influenced by the motion of the electrons. We shall now consider the effect of one on the other and the quantum numbers which characterize the rotational levels in the various types of electronic states.

A molecule has four different sources of angular momenta which are due to (i) the motion of the electron in the orbit, (ii) electron spin, (iii) one or both of the nuclei spinning, and (iv) the rotation of the nuclei as a unit (nuclear rotation). The nuclear-spin angular momentum is often neglected, and the total angular momentum of the molecule may then be regarded as the resultant angular momentum obtained by combining the other three types of angular momenta.

In nearly all diatomic molecules in their ground state the electron spins are paired,[†] and the electron spin angular momentum $S^*h/2\pi$ is zero. Furthermore, the orbit angular momentum $L^*h/2\pi$ of the electrons is also usually zero. Thus, such molecules have a $^1\Sigma$ ground state. If the nuclear spin is neglected, then the only other source of angular momentum of the molecule is that due to nuclear rotation, and the rotational energy equation for such a case was considered in Vol. 2, p. 84.

For free radicals, and certain electronically excited molecules, however, there would be more than one source of angular momentum. Hund was the first to show how these different sources of angular momenta could be coupled together to give a resultant angular momentum. He considered five different cases, known as Hund's cases (a), (b), (c), (d), and (e), in which the resultant angular momentum could be formed.

To appreciate Hund's coupling cases it is necessary to realize that both internal electric and magnetic fields can act along the internuclear axis. The electric field results from the electrostatic field due to the two nuclei. This electric field causes an induced electric dipole to be set up in the molecule which can interact with the electric field and make the orbit angular momentum precess about its axis. Furthermore, as a result of the precession of this orbit angular momentum a magnetic field is set up along the internuclear axis. In addition to these fields a further magnetic field may arise because of the rotation of the nuclei as a pair about their common centre of gravity. This magnetic field acts in the direction of the nuclear angular momentum vector, that is perpendicular to the internuclear axis. For cases where $\Lambda > 0$ and $S > 0$ the interaction between the nuclear angular momentum and the orbit and spin angular momenta of the electrons occurs magnetically.

For each of Hund's cases an equation may be obtained for the rotational energy of the molecule in terms of quantum numbers. All the five cases of Hund are either limiting or extreme cases, and many intermediate cases are found in practice. In general, cases (a) and (b) may be looked upon as the normal coupling cases; these together with case (c) will now be considered.

1.4.2   Hund's case (a)

This applies to diatomic molecules where the internuclear distance is small enough for there to be a sufficiently strong electric field (resulting from the electrostatic field of the two nuclei) along the internuclear axis to prevent $L^*h/2\pi$ and $S^*h/2\pi$ from directly coupling. The electric dipole moment (associated with $L^*h/2\pi$) induced by this electric field then interacts with the electric field and $L^*h/2\pi$ is caused to precess about the internuclear axis and has an angular momentum $\Lambda h/2\pi$ in the direction of the internuclear axis. The precession of $L^*h/2\pi$ sets up a strong magnetic field along the internuclear axis,

[†] The O_2 and NO molecules are exceptions.

which enables the magnetic dipole associated with the electron spin vector to interact, and $S^* h/2\pi$ is also caused to precess about the internuclear axis. The magnetic interaction of the $S^* h/2\pi$ and $\Lambda h/2\pi$ vectors is strong. This results in the $S^* h/2\pi$ vector being strongly coupled to the magnetic field along the internuclear axis so that its axial component $\Sigma h/2\pi$ is quantized. It follows, therefore, that the total angular momentum quantum number Ω along the internuclear axis is given by:

$$\Lambda + \Sigma = \Omega$$

where $\Omega h/2\pi$ is the total electron angular momentum along the internuclear axis.
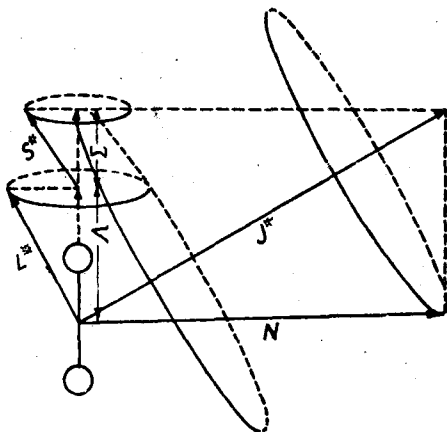

Fig. 1.6 Vector diagram for Hund's case (a) L^*, S^*, Λ, Σ, J^*, and N are each in $h/2\pi$ units.

The precession of $L^* h/2\pi$ and $S^* h/2\pi$ is shown in Fig. 1.6, and their components $\Lambda h/2\pi$ and $\Sigma h/2\pi$, respectively, along the internuclear axis are indicated. The total electron angular momentum about the internuclear axis is well defined. The nuclei in the rigid diatomic molecule may be regarded as rotating as a whole about an axis perpendicular to the internuclear axis and having an angular momentum of rotation $Nh/2\pi$ which will act perpendicular to the centre of gravity of the molecule. If the interaction between $Nh/2\pi$ and $\Omega h/2\pi$ is very weak, then these two angular momenta may be combined vectorially to form a resultant angular momentum:

$$\sqrt{[J(J+1)]}\, h/2\pi$$

where $J = \Omega, \Omega + 1, \Omega + 2, \ldots$.

The precession of various vectors is given in Fig. 1.6, where the vector parallelogram formed from $\Omega h/2\pi$ and $Nh/2\pi$ has been completed with the broken lines, and the resultant total angular momentum is represented by the diagonal. The coupling vectors $\Omega h/2\pi$ and $Nh/2\pi$ precess about the axis of the resultant total angular momentum.