

Orders of Magnitude and Symmetry in Molecular Spectroscopy

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1 INTRODUCTION

A molecule is an aggregate of electrons and nuclei each with a mass, an electric charge, a magnetic dipole moment for the former, and often electric and magnetic multipole moment for the latter. The particles move in a very complicated manner in the electric and magnetic fields. If the system were governed by the law of classical mechanics, it would be a hopeless task to quantify this complicated system. The three-body problem under the gravitational force alone is already a headache for astronomers. Quantum mechanics makes it simpler. The quantum mechanics of molecules is manageable for two reasons. First, because of *the principle of superposition of states*, which is the subject of the first chapter of Dirac (1986) as “one of the most fundamental and drastic departure from classical mechanics”, magnetic moments of two electrons paired in a singlet state are canceled so perfectly that we can completely forget about their magnetic interaction. For an ordinary stable molecule where electrons are all paired, we need to consider only the electric interactions of electrons. For a radical or a molecule in a multiplet state like O₂ we need to consider only the magnetic effect of electrons in the multiplet state, and do not need to consider their magnetic interactions with other paired electrons. The principle of superposition of states also reduces the classically chaotic motion to simple linear combinations of eigenfunctions and makes the problem manageable.

Second, the two dimensionless quantities, the fine structure constant (Section 2.1), $\alpha = e^2/\hbar c \sim 1/137$, and the

Born–Oppenheimer constant (Section 2.3), $\kappa = (m/M)^{1/4} \sim 1/10$, are both much smaller than 1 and we can treat many interactions using the perturbation method as a power series of α and κ with good convergence. Nuclear physics and particle physics do not have this advantage since, for the strong interaction, the corresponding dimensionless number $g^2/\hbar c$ is larger than 1 and the perturbation method cannot be applied effectively. In Section 2, we enumerate all possible atomic and molecular interactions, express them in a power series of α and κ and estimate their orders of magnitude. Although not mentioned in previous textbooks of molecular spectroscopy, it is believed that the consideration of orders of magnitude of various interactions is one of the foundations of molecular spectroscopy. The author has learnt the importance of estimating the order of magnitude both in theory and experiment as a student of Shimoda (1960), his thesis supervisor, to whom this chapter is dedicated.

The other foundation is molecular symmetry which is discussed in Section 3 of this chapter. Discussions of symmetry using group theory is useful for gaining perspective in many fields of science, but it is particularly rich and multifaceted in molecular spectroscopy because it contains the rigorous symmetry for permutation of identical nuclei. This is almost unique for free molecules. Traditionally, molecular symmetry has been discussed on the basis of geometrical symmetry using point groups because the symmetry entered molecular spectroscopy through crystallography (Section 3.2.2), but clearly the symmetry of permutation is more rigorous and allows more direct discussions.

While the discussion of the order of magnitude in Section 2 is quantitative but approximate, that of symmetry in Section 3 is qualitative but rigorous. They are closely

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related and they together make molecular spectroscopy transparent and tidy. Unlike the order of magnitude, the molecular symmetry has been discussed in many textbooks of molecular spectroscopy. Here, the discussions are limited to the most fundamental ones. The symmetries of the electronic and vibrational states are discussed in the classic books by Herzberg (1989) and Wilson *et al.* (1980) and the discussions are limited only to the symmetry of rotational states that are not fully discussed in the previous textbooks.

2 ORDERS OF MAGNITUDE OF VARIOUS INTERACTIONS

2.1 The Fine Structure Constant

In our theory of the fine structure there is a confluence of the three main currents of modern research in theoretical physics, namely, the theory of electrons [e], the theory of quanta [$h/2\pi$], and the theory of relativity [c]. This is exhibited in a particularly vivid way in the way our fine-structure constant is built up: $\alpha = 2\pi e^2/hc$.

Sommerfeld (1919)

All molecular quantities can be described by four natural constants – the elementary electric charge e , Planck's constant h , the light velocity c , the mass of the electrons m – and nuclear parameters such as their mass M , electric charge Ze , and electric and magnetic multipole moments. The nuclear parameters should also be reducible to a few natural constants but this is more difficult for the reason mentioned earlier. Here, we treat them as given constants. As mentioned above by Sommerfeld, who introduced the fine structure constant, each of the natural constant represents a major field of modern physics: e – electrodynamics, h – quantum mechanics, and c – special relativity. If a formula contains a natural constant, you are assured that the field of physics represented by the constant has been used in its derivation.^a The gravitational interaction represented by G , which plays the dominant role in astronomy, also exists in atoms and molecules, but since $GM_p^2/e^2 \sim 8.1 \times 10^{-37}$, its effect is negligible compared with the electric interaction for the currently available spectroscopic techniques.

From the three universal constants, e , h , and c , we can form a dimensionless quantity, Sommerfeld's fine structure constant, central to the atomic theory and quantum electrodynamics,

$$\alpha = \frac{e^2}{\hbar c} \sim \frac{1}{137.03599968} \quad (1)$$

where \hbar is Dirac's $h/2\pi$. It is believed that someday this value will be explained by a deep theory but for now, we just accept it as a constant.

The meaning of the fine structure constant is seen most directly from Bohr's model of hydrogen atom. For the electron at a distance r from the proton moving with a velocity v , the balance of the electric attractive force and the centrifugal force gives

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \quad (2)$$

The 1913 statement of Bohr “[i]f we therefore assume that the orbit of the stationary state is circular, the result of the calculation can be expressed by the simple condition: that the angular momentum [a]round the nucleus in a stationary state of the system is equal to an entire multiple of a universal value [\hbar]” gives

$$rmv = n\hbar \quad (3)$$

Multiplying equations (2) and (3), we have, for $n = 1$,

$$\alpha = \frac{e^2}{\hbar c} = \frac{v}{c} \sim 10^{-2} \quad (4)$$

that is, the fine structure constant gives the order of magnitude of the ratio of velocity of the electron to the velocity of light for low n . The velocity of the electron must be on the order of $v \sim \alpha c \sim 3000 \text{ km s}^{-1}$. The energy of the electron in a hydrogen atom is obtained as

$$W_{\text{elec}} = \frac{mv^2}{2} - \frac{e^2}{r} = -\frac{mv^2}{2} = -\frac{me^4}{2\hbar^2} \cdot \frac{1}{n^2} = -\frac{Ry}{n^2} \quad (5)$$

where n is the principle quantum number and $Ry/hc = 109737.31568527(73) \text{ cm}^{-1}$ is the Rydberg constant. Bohr's old quantum mechanics has been superseded by the quantum mechanics of Heisenberg, Dirac and Schrödinger, and equation (3) is incorrect (n is the principal quantum number and not the angular momentum quantum number), but the energy expression equation (5) and the Bohr radius $a_0 = \hbar^2/me^2 = 0.5291772108 \text{ \AA}$ are identical to those obtained by the new quantum mechanics. The simplicity of Bohr's model allows us to estimate the order of magnitude of many interactions without losing sight in complicated formalism.

Since all relativistic effects of electrons, that is, the magnetic interaction, the retardation effect, the quantum electrodynamical effects etc., scale with v/c , their magnitudes are given as a power series of α . For example, the Einstein energy formula applied to an electron gives

$$W = \frac{mc^2}{\sqrt{1-v^2/c^2}} = mc^2 \left[1 + \frac{1}{2}\alpha^2 + \frac{3}{8}\alpha^4 + \dots \right] \quad (6)$$

The first term is the electron rest mass energy (0.5 MeV). The second term is the kinetic energy, which is equal in

magnitude to the Rydberg constant, and gives W_{elec} when combined with $-e^2/r$. It is shown below that the third term gives magnetic energy, which causes fine structure of atomic spectra.

Finally, we note that the order of magnitude of the electronic energy $W_{\text{elec}} \sim 10\,000 \text{ cm}^{-1}$, the electron velocity $v \sim 3000 \text{ km s}^{-1}$, and the radius $r \sim 0.5 \text{ \AA}$ apply also for atoms with more than one electron and molecules. We are interested in the general order of magnitude discussions and do not worry about differences by a factor of several.

2.1.1 Atomic Interactions

In this section, we enumerate all interactions in atoms that are relevant to spectroscopy and estimate their orders of magnitude. The estimated values for atoms work also for molecules. We are concerned only with a few electrons in the outer shells. Electrons in the inner shells of heavy atoms may have relativistic velocities for which $v/c \gg \alpha$, but their spectra appear in the X-ray region and are outside the scope of this chapter.

2.1.2 Fine Structure

The fine structure of a spectrum is caused by magnetic (relativistic) interactions represented by the third term of equation (6). Again, we start from the simplest case of the H atom for which the rigorous relativistic energy formula is known, but first let us enumerate magnetic interactions using Bohr's model to have a rough picture. There is no such thing as magnetic charge and all magnetic interactions result from relativistic effects due to time-dependent electric fields (the Maxwell theory of electricity and magnetism). Since magnetic effects scale with v/c , a magnetic quantity is α times the corresponding electric quantities. The electric field of the proton at the position of the electron in the Bohr model is

$$E = \frac{e}{a_0^2} = \frac{m^2 e^5}{\hbar^4} \sim 5 \times 10^9 \text{ V cm}^{-1} \quad (7)$$

and the electron moving in this field "feels" a magnetic field of

$$H = \alpha E = \frac{m^2 e^7}{\hbar^5 c} \sim 4 \times 10^9 \text{ G} \quad (8)$$

The electric dipole moment of the H atom is

$$\mu_e = a_0 e = \frac{\hbar^2}{m e} = 2.543 \text{ Debye} \sim 1.3 \text{ MHz V}^{-1} \text{ cm} \quad (9)$$

and the magnetic dipole moment of the orbital motion of the electron is

$$\mu_B = \frac{1}{2} \alpha \mu_e = \frac{e \hbar}{2 m c} \sim 1.4 \text{ MHz G}^{-1} \quad (10)$$

which was named the Bohr magneton by Pauli in 1920. The factor of 1/2 is due to the definition of the magnetic moment. Dirac's relativistic wave equation for the electron, which does not contain any ad hoc magnetic parameter but simply uses the quantized operator form of the electron energy given in equation (6), gives the spin angular momentum s and its magnetic moment whose magnitude is also μ_B . Therefore the magnetic (relativistic) energy of the electron moving with the orbital angular momentum l in the electric field is

$$W_{s,l} = \mu_B H = \frac{m e^8}{2 c^2 \hbar^4} = \alpha^2 R y \sim 10 \text{ cm}^{-1} \quad (11)$$

Just like the nonrelativistic energy of the electron in the H atom is given rigorously by the Bohr formula equation (5), the relativistic energy of the electron is given by the solution of Dirac's relativistic wave equation with the Coulomb potential $-e^2/r$. The solution is

$$W = m c^2 \left[1 + \left\{ \frac{\alpha}{n - (j + \frac{1}{2}) + \sqrt{(j + \frac{1}{2})^2 - \alpha^2}} \right\}^2 \right]^{-\frac{1}{2}} \quad (12)$$

where j is the quantum number for the total angular momentum, $j = l + s$. Readers are referred to Dirac (1986) for the Dirac equation and Bethe and Salpeter (1977) for a derivation and history of the solution (12). Expanding equation (12), we have

$$W = m c^2 \left[1 - \frac{1}{2} \alpha^2 + \frac{3}{8} \alpha^4 \left\{ 1 - \frac{4}{3(j + \frac{1}{2})} \right\} - \dots \right] \quad (13)$$

which mimics equation (6) with $-e^2/r$ added because of equation (5). The third term for an arbitrary value of n can be rewritten as

$$W_{s,l} = \frac{\alpha^2 R y}{n^4} \left[\frac{3}{4} - \frac{n}{j + \frac{1}{2}} \right] \quad (14)$$

which is the expression given by Sommerfeld using old quantum mechanics. Note the agreement in the order of magnitude with equation (11). The fine structure splitting between the $2^2 P_{3/2}$ and $2^2 P_{1/2}$ levels of hydrogen is 0.3652 cm^{-1} , which is about 30 times smaller because $n = 2$ and from other quantum number dependencies. This is special for the H atom because of an extra degeneracy ("accidental" degeneracy, see Vol. III of Landau and Lifshitz^b). For other atoms and molecules, the spin-orbit interaction is on the order of 10 cm^{-1} as given

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in equation (11). The order of magnitude discussed in this chapter is for the coefficient and applies to energy for low quantum numbers.

The energy of the spin-orbit interaction $W_{s,l}$ considered above for the electron in the H atom is between the spin angular momentum s and the orbital angular momentum l of the *same* electron. For other atoms and molecules containing more than one electron, sometimes we need to consider magnetic interactions between different electrons. Energies of spin-other-orbit interaction $W_{s,l'}$ and spin-spin interaction $W_{s,s'}$ (where the prime signifies a different electron) are both on the same order of magnitude as $W_{s,l}$, that is

$$W_{s,l} \sim W_{s,l'} \sim W_{s,s'} \sim \alpha^2 Ry \sim 10 \text{ cm}^{-1} \quad (15)$$

This is most directly seen from the fact that both the orbital angular momentum l and spin angular momentum s' of the other electron have magnetic moments on the order of μ_B and the magnetic interaction with s is on the order of the dipole-dipole interaction, μ_B^2/a_0^3 .

2.1.3 Radiative Corrections

Since the relativistic energy expression (12) depends only on quantum numbers n and j but does not depend on l , the $2S_{1/2}$ and $2P_{1/2}$ levels of H should be degenerate. Early high-resolution optical spectroscopy hinted that this was not the case and that equation (12) was not the final word. Pasternack interpreted it as due to a shift of the $2S_{1/2}$ level and it was called the *Pasternack effect*. Lamb and Retherford measured the direct radio frequency transition between the two levels at 1057.77 MHz. This measurement together with the discovery that the magnetic moment of the electron is slightly higher than μ_B has led to the development of quantum electrodynamics (QED). Readers are referred to Bethe and Salpeter (1977) for the theory. Here it suffices to mention that the Lamb shift, which is also called a *radiative correction*, is on the order of $\alpha^3 Ry \sim 0.1 \text{ cm}^{-1}$ and it is the only interaction in which an odd power of α appear in the energy formula.

The radiative corrections on the order of 0.1 cm^{-1} applies also to other atoms and molecules. The degeneracy of the S and P levels, however, is unique for hydrogen and hydrogen-like ions ("accidental" degeneracy), and the radiative correction simply shifts nondegenerate energy levels for other atoms and molecules. It is relevant only when an experimental spectrum is compared with very accurate *ab initio* theory.

The radiative correction to the electron spin magnetic moment expressed as the spin g -factor is

$$g_s = 2 \left(1 + \frac{\alpha}{2\pi} - 2.973 \frac{\alpha^2}{\pi^2} + \dots \right) \quad (16)$$

2.1.4 Hyperfine Structure

We now consider smaller interactions due to electric and magnetic multipole moments of atomic nuclei. These moments exist because nuclei are not point charges but have size and shape. Splittings of spectra due to nuclear moments are usually much smaller than the fine structure, hence the name *hyperfine* structure. We first note that a nucleus with the nuclear spin quantum number I has multipole moments up to 2^{2I} -pole, and that the multipole moment is electric if I is an integer but is magnetic if I is a half integer. Thus, monopole 2^0 , quadrupole 2^2 , hexadecapole 2^4 , etc., are electric, while dipole 2^1 , octopole 2^3 , etc., are magnetic. Intensive searches for particles with moments violating this rule such as magnetic monopole, electric dipole have been conducted without success. Thus, for example, ^4He , ^{12}C , ^{16}O , etc., with $I = 0$ have only the electric monopole (charge), ^1H , ^3He , ^{13}C , etc., with $I = 1/2$, have a charge and a magnetic dipole, ^2H , ^6Li , ^{14}N , etc., with $I = 1$ have a charge, a magnetic dipole, and an electric quadrupole, and so on.

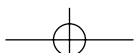
The expression of the Bohr magneton equation (10) shows that a magnetic moment of a particle is inversely proportional to its mass. Thus, the magnetic dipole moments of nuclei are smaller than that of an electron by $m/M \sim \kappa^4 \sim 10^{-4}$. It is on the order of the nuclear magneton

$$\mu_N = \frac{e\hbar}{2M_p c} \sim 0.7623 \text{ kHz G}^{-1} \quad (17)$$

and the individual magnetic moment of a nucleus is expressed by a g -factor, $\mu_m = g\mu_N$. The g -factor of a nuclear magnetic moment cannot be expressed as neatly as for electron for the reason mentioned earlier but g is on the order of 1 (e.g., 2.7285 for ^1H , 0.85744 for ^2H , 0.70241 for ^{13}C , etc.). Thus, the energies of the (nuclear spin)-(electron spin) interaction $W_{I,s}$ and the (nuclear spin)-(electron orbit) interactions $W_{I,l}$ are both on the order of

$$W_{I,s} \sim W_{I,l} \sim \kappa^4 W_{s,l} \sim \kappa^4 \alpha^2 Ry \sim 10^{-3} \text{ cm}^{-1} \sim 30 \text{ MHz} \quad (18)$$

The accurate formula for $W_{I,s}$ for the H atom was derived by Fermi using a perturbation treatment of the Dirac equation with the nuclear magnetic vector potential $U = [\boldsymbol{\mu} \cdot \mathbf{r}]/r^3$. The hyperfine splitting between the two levels $F = 1$ and 0, in which s is parallel and antiparallel to l were derived as $8\pi g\mu_N\mu_B |\psi(0)|^2$ where $|\psi(0)|^2$ is the probability of finding the electron at the position of the nucleus (the Fermi contact term). For the H atom, this term which is nonvanishing only for S electrons ($l = 0$), can be combined with the nuclear spin-electron orbit interaction,



which is nonvanishing for other electrons in a formula,

$$\Delta W_{I.s} = g \frac{m}{M_p} \alpha^2 R_y \frac{2(2j+1)}{n^3(2l+1)j(j+1)} \quad (19)$$

Readers are referred to Bethe and Salpeter (1977) for derivation and more discussions of the interaction. For the H atom, the splitting between the $F = 1$ and 0 spin state appears at 1420.405752 MHz (the famous 21-cm line), which is considerably higher than $\alpha^2 \kappa^4 R_y$ because m/M_p is much higher than 10^{-4} , $g \sim 2.73$, and because of the quantum number dependence.

For nuclei with $I \geq 1$, observable hyperfine splittings are produced by the nuclear electric quadrupole interaction whose order of magnitude is estimated as follows. The size of a nucleus has been observed to be on the order of the classical electron radius,

$$r_0 = \frac{e^2}{mc^2} = 2.818 \times 10^{-13} \text{ cm} \quad (20)$$

the distance from the center to the point at which the magnitude of the Coulomb energy is comparable to the electron rest mass energy. Comparing this with the expression of the Bohr radius a_0 , we note

$$r_0 = \alpha^2 a_0 \quad (21)$$

The electrostatic potential theory shows that the electric charge e , the dipole moment $\mu \sim er$, the quadrupole moment $Q \sim er^2$, etc., interact with the electric potential $\varphi \sim e/r$, the electric field $E = -\nabla\varphi \sim e/r^2$, the electric field derivative $\nabla \cdot E \sim -2e/r^3$, etc., respectively (Landau and Lifshitz Vol. II). Energy of the electric quadrupole interaction is

$$W_{eqQ} = \frac{1}{3!} \sum_{\alpha\beta} Q_{\alpha\beta} \frac{\partial^2}{\partial\alpha\partial\beta} \cdot \frac{e}{r} \sim er_0^2 \cdot \frac{e}{a_0^3} \sim \alpha^4 R_y \sim 10^{-3} \text{ cm}^{-1} \sim 30 \text{ MHz} \quad (22)$$

that is, comparable to $W_{I.s}$. Since nuclei have a wide range of charge and shape, the actual quadrupole coupling constant eqQ (q for the field gradient of electron distribution and Q for the nuclear quadrupole moment) varies widely from a high value of ^{127}I (~ 2000 MHz) to a low value of ^2H (< 0.2 MHz). Similar arguments show that the order of magnitude of the magnetic octopole interaction and the electric hexadecapole interactions are on the order of $\sim \alpha^6 \kappa^4 R_y$ and $\sim \alpha^8 R_y$, respectively, which are both on the order of $10^{-11} \text{ cm}^{-1} \sim 3 \text{ Hz}$ and are negligible in the context of this chapter. The order of magnitude of hyperfine structure discussed in this section applies also for molecules.

2.2 Molecular Interactions

It will be shown that the known magnitude of molecular terms corresponding to the energy of electronic motion, nuclear vibration and rotation can be obtained as terms of a power series expansion in the fourth root of the ratio of the electron mass to (average) nuclear mass.

Born and Oppenheimer (1927) *Ann. Phys.* **84**, 457

2.2.1 The Born–Oppenheimer Constant

The atomic interactions discussed in the previous section also occur in molecules, and their orders of magnitude are comparable in atoms and molecules. A molecule has additional motion of vibration and rotation and their interactions with electrons. The Born–Oppenheimer constant

$$\kappa = \left(\frac{m}{M}\right)^{\frac{1}{4}} \sim 10^{-1} \quad (23)$$

plays the central role in sorting out their orders of magnitude. Since M is an “average” nuclear mass, κ is not a unique number like α . For example, it is 0.15274, 0.08223, and 0.06093 for ^1H , ^{12}C , and ^{32}S , respectively, but it is on the order of 0.1. Like α , someday the values of m/M_p etc., will be explained but for now we just use them as constants.

2.2.2 Rotation and Vibration

We first recall that Planck’s constant h has the dimension of action $\int pdq$ and angular momentum (angular action) $\mathbf{r} \times \mathbf{p}$. It is the action and angular momentum that is quantized to \hbar ; the quantization of energy is secondary. The angular momentum is on the order of \hbar for low quantum number regardless of motion. The angular momentum of an electron rmv and molecular rotation RMV_r are both on the order of \hbar . Since for a small molecule, electronic orbital radius r is comparable to internuclear distance R , we have $mv \sim MV_r$, that is, the nuclear velocity of rotational motion is on the order of $V_r \sim \kappa^4 v \sim \kappa^4 \alpha c \sim 300 \text{ m s}^{-1}$, comparable to the sound velocity. Thus, for a low rotational quantum number, the order of magnitude of the rotational energy is

$$W_{\text{rot}} \sim \frac{1}{2} M V_r^2 \sim \kappa^4 R_y \sim 10 \text{ cm}^{-1} \quad (24)$$

comparable to the spin–orbit and spin–spin interaction of electrons. This gives the order of magnitude of rotational constants of simple molecules.

The energy of molecular vibration is expressed in terms of force constant k , amplitude of vibration δR , reduced mass μ , and nuclear velocity of vibration V_v as

$$W_{\text{vib}} = k(\delta R)^2 = \mu V_v^2 \quad (25)$$

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where the virial theorem is used. If δR is made comparable to the internuclear distance R , the potential energy becomes comparable to the dissociation energy, which is on the order of W_{elec} , that is,

$$|W_{\text{elec}}| \sim \frac{1}{2}kR^2 \sim \frac{1}{2}mv^2 \quad (26)$$

Using these two formulae together with quantization of action, $\mu V_v \delta R \sim mvr \sim \hbar$, and $r \sim R$, and $\mu \sim M$, we have

$$V_v \sim \kappa^3 v \sim 3 \text{ km s}^{-1} \text{ and } W_{\text{vib}} \sim \kappa^2 Ry \sim 1000 \text{ cm}^{-1} \quad (27)$$

which appears in the infrared. We also see that $\delta R \sim \kappa R$ and $V_r \sim \kappa V_v$.

There is an important interaction between vibration and rotation in polyatomic molecules called the *Coriolis* interaction (Teller and Tisza 1932). This is due to the apparent Coriolis force because of vibrational motions in the rotating molecular frame. The magnitude of this effect as an operator is on the order of the rotational energy, i.e., $\sim \kappa^4 Ry$.

The original nonrelativistic molecular Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_n \frac{\hbar^2}{2M_n} \nabla_n^2 + \sum_{i>j} \frac{e^2}{|r_i - r_j|} + \sum_{m>n} \frac{Z_m Z_n e^2}{|R_m - R_n|} - \sum_{n,i} \frac{Z_n e^2}{|R_n - r_i|} \quad (28)$$

After solving and separating the electronic Hamiltonian, we obtain the general and rigorous Wilson–Howard–Watson Hamiltonian (Wilson and Howard 1936, Watson 1968) for the vibration and rotation,

$$\hat{H} = \frac{\hbar^2}{2} \sum_{\alpha,\beta} \mu_{\alpha\beta} (J_\alpha - \pi_\alpha)(J_\beta - \pi_\beta) + \frac{1}{2} \sum_k P_k^2 - \frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha} + V \quad (29)$$

where $\mu_{\alpha\beta}$ are components of the effective reciprocal moment of inertia tensor $\boldsymbol{\mu}$ and π_α and π_β are components of vibrational angular momentum $\boldsymbol{\pi}$. The Coriolis interaction is contained in equation (29) as the coupling (product) of rotational angular momentum \boldsymbol{J} and vibrational angular momentum $\boldsymbol{\pi}$.

The moment of inertia tensor \boldsymbol{I} , and thus its effective inverse $\boldsymbol{\mu}$ is a function of vibrational coordinates. Since $\delta R/R \sim \kappa$, the first term of equation (29) can be expanded in an infinite power series of vibrational coordinates whose orders of magnitude scales with the power of κ (Oka 1967). A perturbation treatment of the first term in the

expansion gives the centrifugal distortion correction. Since the order of magnitude of the first term is $\sim \kappa W_{\text{rot}} \sim \kappa^5 Ry$ and the vibrational separation is $\sim \kappa^2 Ry$, the second-order perturbation gives the quartic centrifugal distortion constant on the order of $\kappa^8 Ry \sim 30 \text{ MHz}$.

Near the equilibrium, the vibrational potential V in equation (29) can also be expanded in terms of dimensionless normal coordinates as

$$\hat{V} = \frac{1}{2} \sum_k \omega q_k^2 + \frac{1}{3!} \sum_{klm} k_{klm} q_k q_l q_m + \frac{1}{4!} \sum_{klmn} k_{klmn} q_k q_l q_m q_n + \dots \quad (30)$$

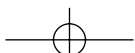
where the terms have orders of magnitude $\kappa^2 Ry$, $\kappa^3 Ry$, $\kappa^4 Ry$, . . . This hierarchy in the order of magnitude allows for a systematic treatment of vibration–rotation interactions by perturbation theory, or contact transformation. Extensive results up to the fourth-order perturbation, applicable in general to all molecules with small amplitude of vibration, are given by Aliev and Watson (1985). The orders of magnitude of all terms as operators follow the rule that the vibrational operator p and q carry the magnitude κ and the rotational operator \boldsymbol{J}^2 carries the magnitude κ^4 (it is discussed later that odd powers of \boldsymbol{J} cannot appear in the Hamiltonian unless it is coupled with electronic or vibrational angular momentum because of the time reversal symmetry). Thus we see that the order of magnitude of vibrational frequency ν , rotational constant B , vibration–rotation constant α and ℓ -type doubling constant q_ℓ , quartic centrifugal distortion constant D , sextic centrifugal constant H , etc., are $\kappa^2 Ry$, $\kappa^4 Ry$, $\kappa^6 Ry$, $\kappa^8 Ry$, $\kappa^{12} Ry$, respectively. The first-order Coriolis interaction is on the order of $\kappa^4 Ry$, while in the second order it is $\kappa^6 Ry$. This rule applies, in general, to the dependence on vibration and rotation of operator for any physical quantity f . Thus for a series expansion,

$$\hat{f} = f_e + \sum_k f_k q_k + \frac{1}{2} \sum_{kl} f_{kl} q_k q_l + \frac{1}{3!} \sum_{klm} f_{klm} q_k q_l q_m + \frac{1}{4!} \sum_{klmn} f_{klmn} q_k q_l q_m q_n + \dots + \sum_{\alpha\beta} f_{\alpha\beta} J_\alpha J_\beta + \dots \quad (31)$$

the order of magnitude of the coefficients f_e , f_k , f_{kl} , f_{klm} , f_{klmn} , and $f_{\alpha\beta}$ are f , κf , $\kappa^2 f$, $\kappa^3 f$, $\kappa^4 f$, and $\kappa^4 f$, respectively, unless they are forbidden by symmetry.

The energy of diatomic molecules is expressed in Dunham's series,

$$W = \sum_{l,j} Y_{lj} \left(v + \frac{1}{2} \right)^l [J(J+1)]^j \quad (32)$$



which is slightly modified from the original expression in that the electronic energy is incorporated in Y_{00} for convenience. Since $\langle(p^2 + q^2)/2\rangle = (v + 1/2)$, the above rule shows that the order of magnitude of Y_{lj} is $\kappa^{2l+4j}R_y$.

2.2.3 Nuclear Magnetic Interactions

The orders of magnitude of fine and hyperfine interactions discussed for atoms apply equally to molecules although for ordinary molecules all electrons are paired and fine structure does not appear. This applies also for protonated ions such as H_3^+ , H_3O^+ , NH_4^+ , CH_5^+ , other important cation like CH_3^+ , and anions such as OH^- , NH_2^- , etc. Fine structure needs to be considered only for radicals and ions with unpaired electrons, for electronic-excited multiplet states, or for some exceptional cases when the ground state is a multiplet. Ordinary molecules have extremely small magnetic interactions related to nuclear magnetic moments.

The rotational motion of molecules introduces a rotational magnetic moment μ_{rot} that does not exist for atoms. It results from an imbalance of the negative magnetic moment due to electrons and the positive moment due to nuclei. They do not balance even in neutral molecules since the magnetic moment μ_{rot} is proportional to $er^2\omega/2c$, where ω is the angular velocity vector of molecular rotation, and the value of $\langle r^2 \rangle$ is different for electrons and nuclei. Since $r^2\omega \sim \hbar/M$, μ_{rot} is on the order of the nuclear magneton. We therefore have the extremely small (nuclear spin)–rotation interaction,

$$W_{I,J} \sim W_{I,I} \sim \kappa^8 \alpha^2 R_y \sim 10^{-7} \text{ cm}^{-1} \sim 3 \text{ kHz} \quad (33)$$

The direct and indirect $I \cdot I$ interactions $W_{I,I}$ for molecules with more than one nucleus with $I \geq 1/2$ are also on this order of magnitude as seen from $W_{I,I} \sim \mu_N^2/a_0^3$. This miniscule hyperfine structure is observable only by ultrahigh resolution spectroscopy in the gas phase or in NMR spectroscopy (where the indirect $I \cdot I$ interaction appears as chemical shift). However, the smallness of these interactions compared to rotational energy (10^{-8}) has a far reaching important implication in symmetry classification of molecular terms and stability of spin modifications as seen below and in the next section on symmetry.

Molecules in multiplet states have (electron spin) – (nuclear spin) and (electron spin) – rotation interaction which are on the order of

$$W_{I,s} \sim W_{J,s} \sim \kappa^4 \alpha^2 R_y \sim 10^{-3} \text{ cm}^{-1} \sim 30 \text{ MHz} \quad (34)$$

2.2.4 Mixing of Eigenfunctions

Finally we discuss orders of magnitude of Hamiltonian for interactions of different motion and their effect in

mixing eigenfunctions. We have already discussed the vibration–rotation interaction above. For simplicity, we limit the discussions only to molecules where all electrons are paired and there is no magnetic interaction of electrons. Born and Oppenheimer separated the total Hamiltonian into electronic, vibrational, and rotational parts. We add the nuclear magnetic effect to this and write

$$\hat{H} = \hat{H}_e + \hat{H}_v + \hat{H}_r + \hat{H}_n \quad (35)$$

We have seen that orders of magnitude of the terms are in the ratio of $1:\kappa^2:\kappa^4:\kappa^8\alpha^2$.

If the Hamiltonian terms are completely separated as above, the total eigenfunction for a quantum state is simply a product of eigenfunctions for the individual Hamiltonian

$$\psi_{total}^0 = \psi_e^0 \psi_v^0 \psi_r^0 \psi_n^0 \quad (36)$$

For actual molecules, however, the terms are not completely separable; there are terms such as the vibronic interaction, \hat{H}_{ev} , which depends both on the electronic variables and vibrational variables, the vibration–rotation interaction, \hat{H}_{vr} , and the rotation–(nuclear spin) interaction, \hat{H}_{rn} . The orders of magnitude of those mixing terms are equal to that of Hamiltonian with lower energy; thus magnitude of \hat{H}_{ev} , \hat{H}_{vr} , and \hat{H}_{rn} are on the order of $\kappa^2 R_y$, $\kappa^4 R_y$, and $\kappa^8 \alpha^2 R_y$, respectively. We ignore other mixing terms such as \hat{H}_{er} and \hat{H}_{vn} for simplicity since their effect is minor.

In the presence of the off-diagonal Hamiltonian, the eigenfunctions are no longer a simple product but a linear combination of products. For example, \hat{H}_{vr} introduces a linear combination

$$\psi_v^0 \psi_r^0 + \sum_{v'r'} \frac{\langle v'r' | H_{vr} | vr \rangle}{E_v - E_{v'}} \psi_{v'}^0 \psi_{r'}^0 \quad (37)$$

The coefficient of the second term is on the order of κ^2 for low rotational levels but is much larger for high rotational levels. For the rotation nuclear spin interaction, however, the mixing is extremely small since $\langle r'n' | H_{rn} | rn \rangle / (E_r - E_{r'}) \sim \kappa^4 \alpha^2 \sim 10^{-8}$. Therefore we can write the total eigenfunction as

$$\psi_{total} = \psi_{evr} \psi_n^0 \quad (38)$$

to a very good approximation, where ψ_{evr} may be a complicated linear combination of the product of $\psi_e^0 \psi_v^0 \psi_r^0$ but ψ_n^0 is the pure nuclear spin eigenfunction. This is the essence for the stability of nuclear modifications such as ortho- and para- H_2 , and ortho-, para-, and meta- CH_4 , etc., as we see in the next section. This is also the reason why the symmetry classification separately of ψ_{evr} and ψ_n^0 is so nearly rigorous and useful in molecular spectroscopy.

8 Orders of Magnitude and Symmetry in Molecular Spectroscopy

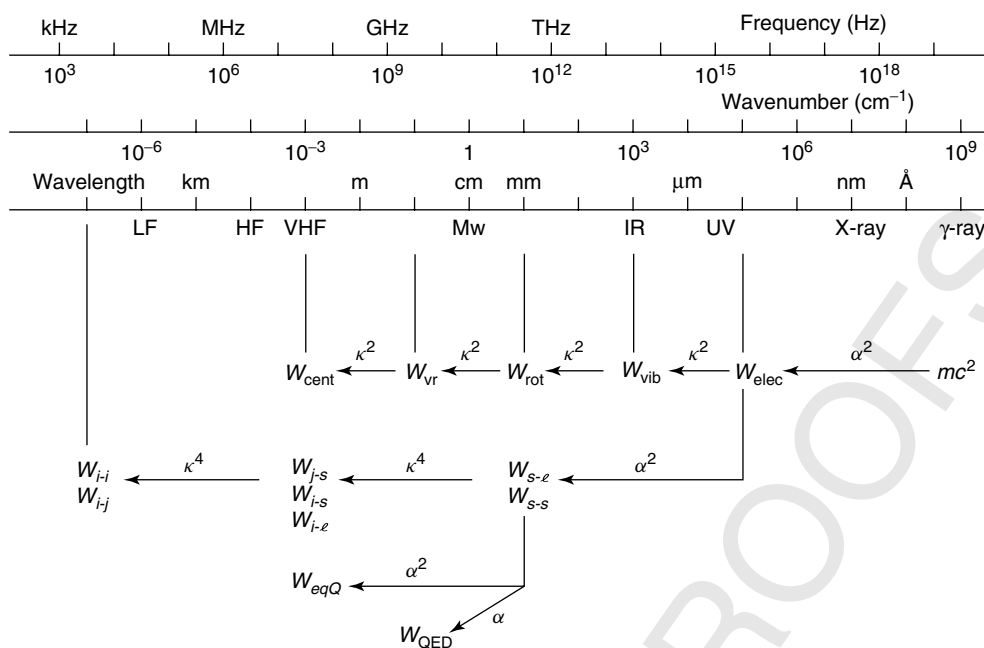


Figure 1 Summary of orders of magnitude of atomic and molecular interactions. W_{vr} stands for vibration–rotation constant α , and ℓ -doubling constant q_ℓ , and W_{cent} stands for quartic centrifugal distortion constant D , D_{JJ} , D_{JK} , Δ , etc.

The discussions given above have dealt with the electronic energy and all couplings of the possible angular momenta, that is, those of electrons (orbital l and spin s), and nuclei (vibrational π , rotational J , and spin I). Those interactions, plus the electromagnetic multipole interaction, exhaust all possible intramolecular interactions. They are summarized in Figure 1 according to their orders of magnitude. A few words of caution are in order.

1. They are order of magnitude estimates. We are not concerned about a discrepancy by a factor of several for higher energies. For lower energies, the estimate can be off by a few orders of magnitude because of individual molecular properties and widely ranging nuclear properties.
2. We are primarily considering small, simple molecules composed of a small number of light nuclei. For heavier molecules vibrational and rotational energies and κ are lower but the expansion in terms of κ remains useful in the systematic treatment of vibration–rotation interactions.
3. The orders of magnitude are for unit quantum numbers. They are for molecular constants. For a high quantum number with $J > 10$, for example, the rotational energy may exceed the vibrational energy.
4. Some of the interactions may not be allowed by symmetry.

Even with the above qualifications, there are exceptions. For example, the ℓ -type doubling constant of H_3^+ is

5.38 cm^{-1} (Oka 1980), which is more like the order of magnitude of rotational constant, because of the small mass and relatively shallow potential surface.

3 SYMMETRY

When we look at a new spectrum, it is the qualitative aspects of the spectrum that strike us first. This is particularly true for plasma (ion and radical) spectroscopy in which we do not know the carrier of a spectrum beforehand. The qualitative fingerprints of the spectrum, its symmetry, regularity and irregularity, intensity alternation and absence of certain lines, multiplicity and fine structure, the presence of hyperfine structure, etc., are the keys to understanding the spectrum and identifying its carrier. These qualitative features are understood by studying the symmetry of molecular Hamiltonian. Such symmetry arguments are useful for atomic spectroscopy but are more explicit and multifaceted in molecular spectra because of the presence of the symmetry of permutation of nuclei.

Unlike the subject of the previous section, molecular symmetry and its application to spectroscopy have been discussed in many textbooks and there is no point repeating them. Here, the discussions are limited to the very fundamental and are not exhaustive. The electronic and vibrational symmetries are discussed in the textbooks by Herzberg (1989) and Wilson *et al.* (1980) and the discussions are limited to rotational symmetry.

3.1 General Remarks

The root of all symmetry principles lies in the assumption that it is impossible to observe certain basic quantities; these will be called 'non-observables'.

Lee (1981)

We begin by stressing that it is not the geometrical symmetry of molecules that primarily concerns us. We are interested in rigorous operations that leave the molecular Hamiltonian invariant. The logical structure of the symmetry argument is well represented by the chart in Figure 2 due to Yang (1958). The symmetry is equal to the invariance. The invariance of a Hamiltonian leads to conservation laws of physical quantities (Noether's theorem). In quantum mechanics, the conservation laws lead to quantum numbers and their selection rules. If the symmetry is rigorous, the corresponding quantum numbers are good and the selection rules are rigorous; if the symmetry is broken by some interaction, the quantum numbers are not good and the selection rules are violated. Readers are referred to Goldstein (1980) for a proof and more details of Noether's theorem.

The following operations leave the molecular Hamiltonian invariant and are relevant for discussion of symmetry in molecular spectroscopy. For each operation, Lee's *nonobservable* is given in parentheses.

1. Continuous space-time symmetry:
 - (a) time translation $t \rightarrow t + \tau$ (absolute time).
 - (b) space translation $\mathbf{r} \rightarrow \mathbf{r} + \boldsymbol{\rho}$ (origin of space).
 - (c) space rotation $\mathbf{r} \rightarrow \mathbf{D}\mathbf{r}$ (absolute direction).
2. Discrete space-time symmetry:
 - (d) space inversion $\mathbf{r} \rightarrow -\mathbf{r}$ (absolute left and right).
 - (e) time reversal $t \rightarrow -t$ (absolute direction of motion).
3. Permutation of identical particles (difference between identical particles).

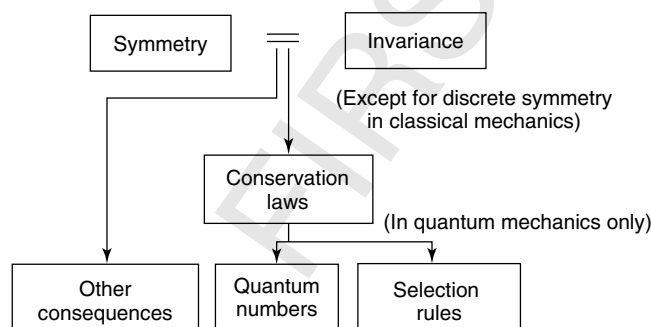


Figure 2 Relation between conservation laws and symmetry laws (Yang 1958).

The matrix \mathbf{D} in (c) is the rotation operator in Eulerian angles. The operations in (1) are continuous in the sense that τ , $\boldsymbol{\rho}$, and \mathbf{D} can take any value.

3.1.1 Continuous Space-time Symmetry

The symmetry of physical laws with respect to the operations (a), (b), and (c) leads to conservation laws of energy, momentum, and angular momentum, respectively. In the history of physics, those invariance and conservation laws have been suspected at times, but never been shown to break down. Readers are referred to Vol. I and III of Landau and Lifshitz for proofs of the conservation laws in classical and quantum mechanics, respectively.

Of the three conservation laws, the conservation of angular momentum due to (c) and its consequences are the most colorful. It appeared first as Kepler's empirical second law of planetary motion: the radius vector sweeps out equal areas in equal times. Newton showed that it is a result of isotropy of the Sun's gravitational field. Conservation and quantization of angular momentum is the cornerstone of quantum mechanics. The orbital angular momentum l of the electron in the hydrogen atom in the isotropic Coulomb potential of the proton is quantized and leads to the azimuthal (l) and magnetic (m) quantum numbers and the spherical harmonics $Y_{lm}(\theta, \phi)$ as its eigenfunction. These eigenfunctions are irreducible representations of the continuous rotation group $SO(3)$.^c

The electron also has spin angular momentum with a value of $\hbar/2$, which was introduced empirically to understand atomic spectra, especially the multiplicity and Zeeman effect, and later shown by Dirac to be a natural consequence of the unification of quantum mechanics and relativity. Readers are referred to Tomonaga (1997) for the history and physics of spin. Unlike the orbital angular momentum whose quantum numbers l, m are integers and may take a large value, the quantum number of electron spin is limited to $s = 1/2$ with its two components $\pm 1/2$. Although initially introduced with a classical image (hence the name *spin*), spin is a purely quantum mechanical concept without classical interpretation and its two-component eigenfunctions follow special mathematics of spinors whose transformation forms the $SU(2)$ group. Readers are referred to Vol. III of Landau and Lifshitz and Lecture 7 of Tomonaga (1997) for spinor algebra. In the context of this book, it suffices to note that, unlike spherical harmonics, the eigenfunction for spin $1/2$ does not come back to original form under rotation of 2π but changes sign and comes back to the original form only after rotation of 4π . Nevertheless, $SU(2)$ is a covering group of $SO(3)$ and we can treat spin operator \hat{s} like orbital angular momentum operator \hat{l} in vector additions. It should also be noted that, unlike orbital angular momentum, which is not good in a molecule due

to lack of spherical symmetry, the integrity of spin angular momentum of an unpaired electron is intact in a paramagnetic molecule. In a nonmagnetic molecule where all electrons are paired, the spin angular momentum and associated magnetic fields completely vanish due to the principle of superposition.

The proton and the neutron also have spin angular momentum I with $I = 1/2$ and their composite atomic nuclei have spins with quantum number I ranging from 0 (^4He , ^{12}C , ^{16}O , ^{20}Ne) to quite high numbers ($I = 7$ for ^{176}Lu). The electron spin and nuclear spin with $I \neq 0$ cause fine and hyperfine structures, respectively, and enrich spectroscopy. However, the most significant and universal effect of spin is the symmetry requirement upon exchange of particles whose consequence pervade all sciences. The permutation symmetry which is discussed later is the central theme of this section.

Isotropy of space also leads to the conservation of angular momentum J of overall molecular rotation and associated quantum numbers. The eigenfunctions are spherical harmonics $Y_{Jm}(\theta, \varphi)$ for linear molecules, the Wigner functions $D_{mk}^J(\varphi, \theta, \chi)$ for symmetric tops, and their arbitrary and specific linear combinations for spherical and asymmetric tops, respectively. Vibrational motion of a molecule causes instantaneous angular momentum $\sum_n \mathbf{r}_n \times \mathbf{p}_n$ some of which is conserved when the molecule has a symmetry axis of more than a twofold rotation. This angular momentum along the symmetry axis is a result of effective cylindrical symmetry of a harmonic oscillation and has vibrational angular momentum quantum number ℓ and the eigenfunction $e^{i\ell\chi}/\sqrt{2\pi}$.

When a system has many angular momenta, they couple in an intricate way, (Vol. III of Landau and Lifshitz), but the total angular momentum is always conserved because of (c). Thus for the H atom the total angular momentum quantum number F for $\mathbf{F} = \mathbf{l} + \mathbf{s} + \mathbf{I}$ is a rigorous quantum number. Since the interaction between the electronic angular momentum $\mathbf{j} = \mathbf{l} + \mathbf{s}$ and the nuclear angular momentum \mathbf{I} , $W_{s,I} + W_{l,I}$, is small, j is a nearly good quantum number. Likewise, for more complicated atoms, F for $\mathbf{F} = \mathbf{L} + \mathbf{S} + \mathbf{I}$ ($\mathbf{L} = \sum_i \mathbf{l}_i$, $\mathbf{S} = \sum_i \mathbf{s}_i$) is a rigorous quantum number while J for $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is a nearly good quantum number. For a molecule, the total angular momentum $\mathbf{R} = \mathbf{J} + \mathbf{S} + \mathbf{I}$ ($\mathbf{I} = \sum_n \mathbf{I}_n$) is rigorously conserved. For an ordinary nonmagnetic ($S = 0$) molecule without a nucleus with $I \geq 1$, the interaction between J and I is extremely small, $W_{I,J} \sim 3$ kHz and J is an almost rigorous quantum number. If isotropy of space (c) is broken by an applied electric or magnetic field, the total angular momentum F gets mixed and ceases to be a rigorous quantum number.

Conservations of total energy, total angular momentum, and other symmetry properties to be discussed in the following sections, such as parity and permutation symmetry, are also useful in dynamical problems where more than one molecule is involved. Readers are referred to Section II C of Oka (1973b) for their application to intermolecular collisions and their selection rules.

Finally, there is an additional continuous space-time symmetry operation, the Lorentz transformation, whose nonobservable is absolute velocity. The Lorentz invariance and symmetry resulting from this transformation, which is central in relativity and electrodynamics, is seldom used in spectroscopy. Readers are referred to Lecture 11 of Tomonaga (1997) for its use in deriving the Thomas precession factor of $1/2$. The invariance is also implicit in any relativistic argument such as the spin-orbit interaction given in Section 2.2.1.

3.1.2 Discrete Space-time Symmetry

Unlike the operations for the continuous space-time symmetry which form Lie (continuous) groups with eigenfunctions as their infinite number of irreducible representations, symmetry operations in this section and the next are discrete and form finite groups whose irreducible representations are simply given by numbers. They are all binary in the sense that, if operated twice, they bring a classical system back to its original state.^d Like positive or negative, left or right, or up or down, they are a “yes or no” type symmetry and are most useful in quantum mechanics where the symmetry of eigenfunctions and operators are to be discussed.

The space inversion $\mathbf{r} \rightarrow -\mathbf{r}$, which will be hereafter denoted by \hat{P} (for parity), reverses polar vectors such as coordinate \mathbf{r} , momentum \mathbf{p} , electric field \mathbf{E} , electric dipole moment $\boldsymbol{\mu}_e$, and current \mathbf{j} , while leaving intact axial vectors such as angular momenta \mathbf{l} , \mathbf{s} , \mathbf{j} , \mathbf{J} , \mathbf{I} , \mathbf{F} , magnetic field \mathbf{H} , and magnetic dipole moment $\boldsymbol{\mu}_m$. The time reversal denoted by \hat{T} reverses quantities involving motion, that is, angular momenta, momentum \mathbf{p} , current \mathbf{j} , magnetic field and dipole moment \mathbf{H} and $\boldsymbol{\mu}_m$, and leaves, \mathbf{r} , \mathbf{E} , and $\boldsymbol{\mu}_e$ intact. Clearly, \hat{P} and \hat{T} leave the Maxwell equation and the spinless molecular Hamiltonian given in equation (28) invariant.

In quantum mechanics, where Euler’s mathematics involving i enters and plays a major role, the operation of time reversal is not quite trivial. The commutation relations $\hat{p}_x x - x \hat{p}_x = \frac{\hbar}{i}$, etc., and the operator equivalence $\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$, etc., which form the basis of quantum mechanics are invariant for $\mathbf{r} \rightarrow -\mathbf{r}$ but not for $t \rightarrow -t$ alone. The quantum mechanical time reversal operator \hat{T} needs to be both $t \rightarrow -t$ and $i \rightarrow -i$. The operator is expressed as $\hat{T} = \hat{U}\hat{K}$ where \hat{U} is a unitary operator for $t \rightarrow -t$ and \hat{K} is a complex-conjugation operator $i \rightarrow -i$. \hat{T} is an antiunitary operator, which does not follow Dirac’s bra and

ket algebra. While $\hat{P}^2 = p^2 \hat{I} = \hat{I}$, where \hat{I} is the identity operator gives parity eigenvalues $p = \pm 1$, $\hat{T}^2 = \pm \hat{I}$ and \hat{T} does not have eigenvalues. Readers are referred to Sakurai (1985) and Sachs (1987) for in-depth discussions of the antiunitary operator and consequences of the time reversal symmetry.

The time reversal invariance requires that a dipole moment of a particle has to be magnetic and cannot be electric as mentioned earlier in Section 2.2.3. Any detection of an electric dipole moment of a particle indicates breakdown of the time reversal symmetry.^e

Use of \hat{T} in molecular spectroscopy is somewhat limited. It is used to find selection rules of matrix elements between degenerate levels (Section 97 in Vol. III of Landau and Lifshitz). Watson's (1974) paper on the condition of the first-order Stark effect (including that for CH₄) with a general theorem involving time reversal is more complete and fertile. \hat{T} is also useful to judge if an operator is allowed as a term in the molecular Hamiltonian. It shows that any expression with odd powers of angular momentum is not allowed. Such term multiplied by i has appeared in the literature (Ozier *et al.* 1970). The term is invariant for \hat{T} but is not Hermitian, that is, its eigenvalue is not real and thus is not allowed.

The inversion operation \hat{P} and its eigenvalue, parity, are central to spectroscopy. It first appeared as Laporte's empirical rule to classify subsets of atomic states of Fe that do not intercombine. All atomic states have unique parities of either +1 or -1 (sometimes we say + or -, or, *even* or *odd*). All physical variables and their quantum mechanical operators have unique parities, and if they are multiplied, the total parity is obtained by simply multiplying the individual parities. Scalars and axial vectors have + parity while polar vectors have - parity. In the molecular Hamiltonian given in equation (28), radial vectors \mathbf{r}_i , \mathbf{R}_n , etc., and the momentum operator ∇_i , ∇_n , etc., have - parity, while $|\mathbf{r}_i - \mathbf{r}_j|$, etc., and ∇_i^2 etc., have + parity resulting in the even parity of the Hamiltonian \hat{H} .

Since the parity operation $\mathbf{r} \rightarrow -\mathbf{r}$ is represented in polar coordinate as $r \rightarrow r$, $\theta \rightarrow \pi - \theta$, and $\phi \rightarrow \phi + \pi$, $\hat{P}Y_{lm}(\theta, \phi) = (-1)^l Y_{lm}(\theta, \phi)$, namely, parity of an atomic orbital eigenfunction is given by $(-1)^l$. For an atom with many electrons, the parity is rigorously given by $(-1)^{l_1+l_2+\dots}$. Spin eigenfunctions have + parity and spin states do not affect the total parity. Together with the total angular momentum quantum number F , the parity is a rigorous quantum number and leads to rigorous selection rules. Intra-atomic interactions $\langle \alpha | \hat{H} | \beta \rangle$ are nonvanishing only between two levels α and β with the same parity, and the electric and magnetic dipole transitions $\langle \alpha | \mu_e | \beta \rangle$ and $\langle \alpha | \mu_m | \beta \rangle$ occur between two states with opposite parities and the same parity, respectively. The parity is central also in molecular spectroscopy and is discussed in Section 3.3.2.

\hat{P} and \hat{T} together with the charge conjugation operation \hat{C} (particle-antiparticle symmetry) form the basis of elementary particle physics. It was shocking news in 1956 when experiments showed that parity is not conserved in the weak interaction. With the unification of electromagnetic and weak interactions it is known that parity is violated in molecules by an extremely small amount. This small effect is probably difficult to detect in nonmagnetic molecules.^f Since the parity violating Hamiltonian is a product of an axial and polar vectors, a free radical with an unpaired electron near the center of chirality may lead to detection of such an effect.

3.1.3 Permutation of Identical Particles

It [spin and statistics] appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation. The explanation is deep down in relativistic quantum mechanics. This probably means that we do not have a complete understanding of the fundamental principle involved.

R. P. Feynman (1966)

The permutation operation of identical particles, (12), is like the parity operation in that $(12)^2 = \hat{I}$ and its eigenvalue is +1 or -1. However, for a system with many identical particles, group theory is needed as we see in the next section. While the \hat{C} , \hat{P} , \hat{T} operations are central in particle physics, the permutation of electrons and that of identical nuclei together with \hat{P} are central in atomic and molecular physics. Especially, the permutation of identical nuclei together with the parity operation is essential for specifying molecular symmetry as discussed in the next section. The concept of identical particle does not exist in classical physics and the permutation symmetry applies only to quantum mechanics. The permutation symmetry of identical particles first appeared in Pauli's (1925) statement, "[t]here can never be two or more equivalent electrons in an atom." It was an ad hoc assumption needed to explain the stability of atoms and Mendeleev's periodic table introduced with an apology "[w]e cannot give a deeper explanation of this rule." In 1926, Heisenberg and Dirac independently represented Pauli's statement as

$$(12)\psi = -\psi \text{ for fermions (particle with half-integer spin)}$$

and

$$(12)\psi = \psi \text{ for bosons (particles with integer spin)} \quad (39)$$

where ψ is the total eigenfunction of a system. The first of these formulae applied to electrons is equivalent to Pauli's statement and Dirac coined the term *Pauli's exclusion principle*. This term, which is sometimes called the *Pauli*

12 Orders of Magnitude and Symmetry in Molecular Spectroscopy

principle is often used to mean the two generalized principles given above in total; we follow this convention.

The symmetry requirement under the (12) operation and its relation to spin is the foundation of the Bose–Einstein statistics and the Fermi–Dirac statistics discovered in 1924 and 1926, respectively. It is the most ingenious design of nature that governs all of science. If the rule ceases to hold, all electrons in atoms would fall down to the $1s$ orbital and there would not be chemical bonds. All electrons in the core of a white dwarf would fall down to the phase space of lowest energy and the stars would become black holes. Its effect is so overwhelming and obvious and yet it is hard to explain. Pauli published his explanation in 1940 and concluded “. . .according to our opinion the connection between spin and statistics is one of the most important applications of relativity theory.” Readers are referred to Tomonaga (1997) and Duck and Sudarshan (1997) for a readable and more in-depth discussion, respectively, on spin and statistics.

Wigner’s Near Symmetry The exchange of two identical nuclei (12) means exchange of the whole set of variables, that is, exchange of coordinates and momenta $(\mathbf{R}_1, \mathbf{P}_1)$ and $(\mathbf{R}_2, \mathbf{P}_2)$, and nuclear spin \mathbf{I}_1 and \mathbf{I}_2 . As is obvious from Figure 3, this operation simply exchanges subscripts 1 and 2, and the whole system is identical physically. Clearly the operation leaves the Hamiltonian invariant. Wigner (1933) noted in the third paper of his trilogy on the general theme of “noncombined terms in the new quantum theory” that “the special stability of para- H_2 is based on a symmetry property of the quantum mechanical energy operator of the

hydrogen molecule; it is not only invariant when the entire set of coordinates of both protons are exchanged but also *nearly invariant* when only the Cartesian coordinates are exchanged leaving the spin coordinates unchanged.” This near symmetry used by Wigner to explain the stability of ortho- and para-spin modifications of H_2 applies to other molecules and we call it *Wigner’s near symmetry*. The operation is shown in Figure 3. For this operation, the system is no longer invariant as for (12) but the difference in energy is extremely small. As shown in the previous section, the difference is on the order of $W_{I,J} \sim W_{I,I} \sim \kappa^8 \alpha^2 R_y \sim 3 \text{ kHz}$, which is smaller than the next hierarchy of molecular energy $W_{\text{rot}} \sim \kappa^4 R_y \sim 10 \text{ cm}^{-1}$ by 10^8 . As shown in the next section, Wigner’s near symmetry is not only the basis of the stability of spin modification (to be discussed in Section 3.3.3) but also the basis of the rigor of overall symmetry classification using the permutation–inversion group.

3.2 Molecular Symmetry Group

3.2.1 Permutation (Symmetric) Group

There exists a well-developed mathematical theory, which one can use here; the theory of transformation groups, which are isomorphic with the symmetric group (the group of permutation).

Wigner (1927)

The concept of permutation symmetry was introduced in attempts to find a general method to solve algebraic equations by Lagrange and Vandermonde and used by Ruffini and Abel to demonstrate unsolvability of quintic equations. Clearly, the equation $\prod_{i=1}^n (x - x_i) = 0$ is invariant for any permutation of x_1, x_2, \dots, x_n , just like the molecular Hamiltonian equation (28) is invariant for any permutation of electrons and identical nuclei. The concept of group was implicit in those works but it was explicitly introduced together with the word “group” by Évariste Galois (1831), barely 19 years old.⁵ After the groundwork by Cauchy, Cayley *et al.*, Frobenius established the representation theory in which each class of symmetry operations is concisely expressed for each symmetry by a *character* in a character table. Group theory was ready for applications in quantum mechanics.

The theory was introduced to quantum mechanics by Wigner (1927), with von Neumann’s advice in the second paper of his trilogy in which the general spinless n -electron problem was studied using the symmetric group S_n . Compared with the first paper of his trilogy submitted only two weeks earlier in which he treated a 3-electron problem without using group theory, the enormous power of the theory in saving work and generalization is obvious.

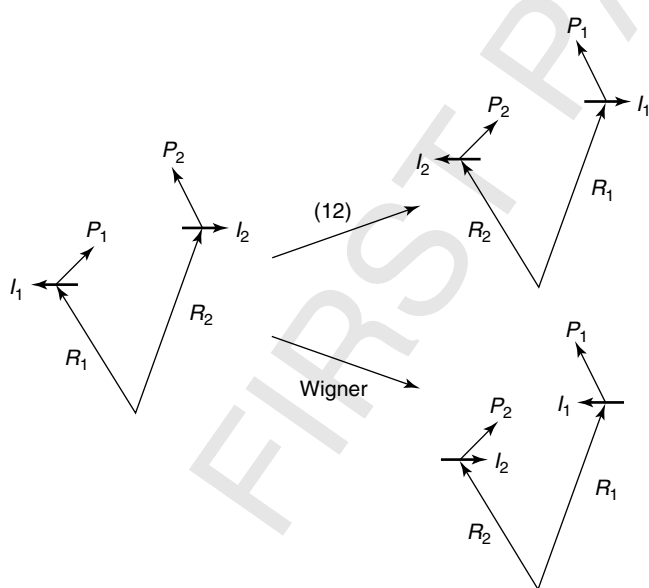


Figure 3 Permutation operation (12) and Wigner’s near-symmetry operation.

Table 1 Character tables of symmetric group S_n . Broken lines separate even and odd permutations.

S_2	l	(12)					
[2]	1	1					
[1 ²]	1	-1					
S_3	l	2(123)	3(12)				
[3]	1	1	1				
[2, 1]	2	-1	0				
[1 ³]	1	1	-1				
S_4	l	8(123)	3(12)(34)	6(1234)	6(12)		
[4]	1	1	1	1	1		
[3, 1]	3	0	-1	-1	1		
[2, 2]	2	-1	2	0	0		
[2, 1 ²]	3	0	-1	1	-1		
[1 ⁴]	1	1	1	-1	-1		
S_5	l	20(123)	15(12)(34)	24(12345)	10(12)	30(1234)	20(12)(345)
[5]	1	1	1	1	1	1	1
[4, 1]	4	1	0	-1	2	0	-1
[3, 2]	5	-1	1	0	1	-1	1
[3, 1 ²]	6	0	-2	1	0	0	0
[2 ² , 1]	5	-1	1	0	-1	1	-1
[2, 1 ³]	4	1	0	-1	-2	0	1
[1 ⁵]	1	1	1	1	-1	-1	-1

Character tables for symmetric groups S_n for $n = 2-5$ are given in Table 1. Classes of operations are given horizontally and irreducible representations vertically. Their numbers are equal and given by number of partitions. For $n = 4$, for example, there are five classes and representations corresponding to the five partitions.

$$4 = 1 + 1 + 1 + 1 \quad 2 + 1 + 1 \quad 2 + 2 \quad 3 + 1 \quad 4 \quad \text{which are expressed as}$$

$$[1^4] \quad [2, 1^2] \quad [2, 2] \quad [3, 1] \quad [4] \quad \text{with operations}$$

$$I \quad (12) \quad (12)(34) \quad (123) \quad (1234).$$

Readers are referred to Hamermesh (1964) for general derivation of the character tables.

Every permutation can be written as a product of transpositions, $(123) = (13)(12)$, $(1234) = (14)(13)(12)$, etc. Depending on the number of transpositions, a permutation is even or odd. Thus I , $(12)(34)$, and (123) are even permutations while (12) and (1234) are odd permutations. All symmetric groups S_n have representation $[n]$ with character 1 for all classes of operation. A function whose transformation is expressed by this representation is called *totally symmetric*. All S_n ($n > 1$) also have alternating representation $[1^n]$ with character +1 for even permutations and -1

for odd permutations. A function that transforms according to this representation is called *totally antisymmetric*. Because of the Pauli principle expressed by equation (39), a total eigenfunction is totally antisymmetric for fermions and totally symmetric for bosons. Thus, if we consider the symmetry of the total eigenfunction, all levels have iden-

tical symmetry, represented either by $[1^n]$ or $[n]$. The rich molecular symmetry classification results when we *separate* the total eigenfunction into rovibronic eigenfunction ψ_{evr} containing cartesian coordinates and the nuclear eigenfunction ψ_n^0 containing spins according to equation (38).

3.2.2 Point Group

Since the crystal is the most symmetric object in nature, it was natural that the idea of symmetry and group theory was first systematically used in crystallography. Around 1850, Auguste Bravais classified crystals systematically

according to their symmetry and this was followed by many mineralogists and mathematicians. The idea of a *point group* based on three-dimensional geometrical operations was introduced, so called because its elements such as the axis of rotation \hat{C}_n , plane of reflection $\hat{\sigma}$, center of inversion \hat{I} , etc., share a point that does not move by the operations. By the end of the nineteenth century, the theory was complete for classifying structures of crystals.

The point group entered quantum mechanics when Bethe (1929) published his paper on the crystal field splitting of atomic levels. For symmetry classification of eigenfunctions, a concept absent in classical physics, he simply used $\Gamma_1, \Gamma_2, \dots$ etc., for increasing order of irreducible representations. The group theory was introduced into molecular spectroscopy when Wigner (1930) used it to classify symmetry of normal vibrations. He used the crystal point group notations such as C_s, C_{2v}, C_{3v}, T_d , etc., to represent groups and E, C_n, σ, S_n , etc., to specify the operations but left blank the column of irreducible representations. Placzek (1934) introduced the currently used symbols of irreducible representations such as A (symmetric), B (antisymmetric), E ("entartet", doubly degenerate), F (triply degenerate), subscript 1 and 2 (to specify symmetry with respect to C_2) and superscript' and '' (to specify symmetry with respect to σ), etc. While a little unsystematic, the much-needed nomenclature was immediately adopted by theorists like Teller, Tisza, Mulliken, Wilson, and others, and has become the fixture in molecular spectroscopy.

Initially, the point group was applied separately to electronic (ψ_e^0), vibrational (ψ_v^0), and rotational (ψ_r^0) eigenfunctions, but Herzberg and Teller (1933) noted that use of the symmetry of coupled vibronic eigenfunctions ψ_{ev} leads to more "strict selection rules". Jahn (1938) also used symmetry of rovibrational eigenfunctions ψ_{vr} in his theory of Coriolis interactions. The symmetry of "overall" eigenfunctions of ψ_{evr} was first systematically given by Landau and Lifshitz (the first version of Vol. III published in 1947), which also included the parity of states. Hougen (1962) showed the basis of the symmetry classification for overall eigenfunctions for small nuclear displacement from equilibrium position, but it was increasingly clear that the point group is not satisfactory for symmetry classifications of overall eigenfunctions especially for molecules with large amplitude of motion in highly excited states, or undergoing inversion and internal rotation. Mulliken (1941) was the first to publish a paper in which symmetry classification by permutation–inversion group is explicitly mentioned and applied to nonlinear AB_2 type molecules. Kasuya (1962) used permutation group for analysis of the microwave spectrum of inverting and internally rotating hydrazine NH_2NH_2 . Longuet-Higgins (1963) systematically introduced the permutation–inversion group,

and the molecular symmetry group, based on rigorous symmetry operations, was established.

3.2.3 Permutation Inversion Group

Permutation inversion groups include direct products of the permutation groups S_n and the parity group $I^* = S_1^*$, i.e., $S_n^* \equiv S_n \times I^* = I^* \times S_n$ with $2n!$ operations and their subgroups S_n^*/q . They are particularly useful for classifying symmetry of molecular ions in which nuclei tend not to stay in their equilibrium positions.

*Direct Product S_n^** Character tables of S_1^*, S_2^* , and S_3^* are given in Table 2. For convenience, the familiar Placzek symbols are used for irreducible representations rather than the partition number used for S_n in Table 1, and they are ordered according to the convention of the point group. Permutation operations $I, (12)$ and (123) , which correspond to rotational operations (proper operations), and permutation–inversion operations $I^*, (12)^*, (123)^*$, which correspond to sense reversing operations (improper operations) and the corresponding symmetry are kept in separate blocks. This arrangement of character tables is similar to that of Wilson *et al.* (1980). However, we use I instead of E for the identity operation following Herzberg. For later use for classifying vibronic eigenfunctions and rotational eigenfunctions, point group operations and rotational operations corresponding to each permutation–inversion operation are also given in the Tables. S_1^*, S_2^* and S_3^* are isomorphic to point groups C_s, C_{2v} and D_{3h} , respectively.

S_2^* is applicable to planar molecules with two identical nuclei such as H_2O, H_2CO , etc. It is also applicable to nonplanar molecules with observable inversion splitting such as NH_2D and H_2DO^+ , and with torsional splitting such as H_2O_2 and H_2S_2 . However, if the barrier to the tunneling motion is high and the splitting is not observable, a subgroup of S_2^* suffices to classify the symmetry (Longuet-Higgins' feasibility of the motion). Thus subgroup $S_2^*/2$ to be discussed below can be used for PH_2D in which, unlike in NH_2D , the inversion splitting is not observable. For H_2S_2 where the torsional splitting is only 58 kHz, S_2 suffices for ordinary spectroscopy but the full S_2^* group is needed for ultrahigh resolution spectroscopy. For a molecule like $HCOOH$, of course, the (12) operation is not feasible and S_1^* suffices.

S_3^* is applicable to planar molecules with three identical nuclei such as H_3^+, CH_3, CH_3^+ , etc. It is also applicable to nonplanar molecules like NH_3, H_3O^+ , etc., with observable inversion splittings. If the inversion splitting is too small to observe as in PH_3 , the subgroup $S_3^*/2$ to be discussed below suffices. An interesting case is protonated acetylene (vinyl cation) $C_2H_3^+$ whose vibrational and rotational spectra are clearly those of a nearly prolate asymmetric top and yet

Table 2 Character tables of full permutation inversion groups S_n^* . Corresponding point group operations and rotational operations, which act on rovibronic and rotational eigenfunctions, respectively, are also listed in the second and the third rows. Vertical broken lines separate proper and improper operations and horizontal broken lines separate + and – parity.

S_1^*	l	l^*				
C_s	l	σ_{XY}				
	l	$C_2(Z)$				
A'	1	1				
A''	1	–1				
S_2^*	l	(12)	l^*	$(12)^*$		
C_{2v}	l	$C_2(X)$	σ_{XY}	σ_{zx}		
	l	$C_2(X)$	$C_2(Z)$	$C_2(Y)$		
A_1	1	1	1	1		
A_2	1	1	–1	–1		
B_1	1	–1	1	–1		
B_2	1	–1	–1	1		
S_3^*	l	$2(123)$	$3(12)$	l^*	$2(123)^*$	$3(12)^*$
D_{3h}	l	$2C_3(Z)$	$3C_2(X)$	σ_{XY}	$2S_3(Z)$	$3\sigma_{zx}$
	l	$2C_3(Z)$	$3C_2(X)$	$C_2(Z)$	$2C_6^{-1}(Z)$	$3C_2(Y)$
A_1'	1	1	1	1	1	1
A_2'	1	1	–1	1	1	–1
E'	2	–1	0	2	–1	0
A_1''	1	1	1	–1	–1	–1
A_2''	1	1	–1	–1	–1	1
E''	2	–1	0	–2	1	0

their tunneling structure demonstrates that the three protons are equivalent due to fast tunneling motions (Gabrys *et al.* 1995). This molecule has two sets of identical nuclei but since the carbon nucleus is a boson with spin 0, they do not affect the symmetry argument. The spectrum can be explained using S_3^* .

Cases for higher S_n^* had not appeared until recent development in molecular ion spectroscopy. S_4^* was used for analysis of the Jahn–Teller effect in the ZEKE spectra of CH_4^+ and CD_4^+ in a seminal paper by Wörner *et al.* (2007). S_5^* is needed for the infrared spectrum of protonated methane, CH_5^+ , in which five equivalent protons are swarming around the central carbon. This is a difficult problem of a new prototype of vibration-rotation-tunneling motion and assignment of the observed spectrum (White *et al.* 1999) will take many decades (perhaps a century). Whether spectral analysis of H_5^+ requires the full S_5^* group or its subgroup $S_3^* \times S_2^*$ suffices depends on the widths of spectral lines. For the highest resolution spectroscopy without predissociation, it will certainly require S_5^* .

Subgroups S_n^*/q For molecules with three equivalent particles like PH_3 and CH_3OH , and those with four equivalent particles such as CH_4 and NH_4^+ , even permutations

are feasible but odd permutations are not, and reverse is the case when combined with the inversion operation I^* . For example, for the S_4^* group, 4! operations, I , $8(123)$, $3(12)(34)$, $6(1234)^*$ and $6(12)^*$ are feasible and other 4! operations are unfeasible. For such a case, a subgroup of S_n^* composed only of feasible operations S_n^*/q suffices where q is the quotient of the order of S_n^* divided by that of the subgroup. For simple molecules mentioned above, $S_n^*/2$ with $n!$ elements and isomorphic to S_n are used; $S_3^*/2$ is isomorphic to the C_{3v} point group and $S_4^*/2$ is to T_d . Their characters are listed in Table 3. For larger molecules, there are more unfeasible permutation–inversion operations and the quotient is higher. For example, $S_4^*/6$ is used for ethylene and $S_6^*/60$ is used for benzene.

3.3 Symmetry of Rotational Levels

3.3.1 Assignment of Symmetry

Total Eigenfunction Hereafter we assume totally symmetric vibronic state and consider only rotational wavefunctions. Symmetry of the total eigenfunction $\psi_{\text{total}} = \psi_r^o \psi_n^o$ is governed by the Pauli principle, which involves the permutation operation only. For S_n^* where the parity operation

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Table 3 Character tables of permutation inversion subgroup $S_n^*/2$ composed of feasible operations.

$S_2^*/2$	l	$(12)^*$			
	l	σ_{xy}			
	l	$C_2(Z)$			
A	1	1			
B	1	-1			
$S_3^*/2$	l	$2(123)$	$3(12)^*$		
	l	$2C_3(Z)$	$3\sigma_{zx}$		
	l	$2C_3(Z)$	$3C_2(Y)$		
A_1	1	1	1		
A_2	1	1	-1		
E	2	-1	0		
$S_4^*/2$	l	$8(123)$	$3(12)(34)$	$6(1234)^*$	$6(12)^*$
	l	$8C_3$	$3C_2$	$6S_4$	$6\sigma_v$
	l	$8C_3$	$3C_2$	$6C_4^{-1}$	$6C_2'$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
F_1	3	0	-1	1	-1
F_2	3	0	-1	-1	1

I^* is feasible, I^* can be considered separately. However, for $S_n^*/2$ where I^* is not feasible, I^* and permutation operations are interwoven and they should be considered simultaneously (Oka 1973a); thus even though the Pauli principle does not specify parity directly, certain parity is required. For brevity we consider, here, only the cases where the identical particles are protons (fermion, $I = 1/2$); extensions to other nuclei are straightforward. For fermions ψ_{total} should be totally antisymmetric, that is, invariant for even permutations and change sign for odd permutations. Thus from character tables we see that the allowed symmetry of ψ_{total} is B_1 and B_2 for S_2^* , A_2' and A_2'' for S_3^* , and $A_2(+)$ and $A_1(-)$ for $S_3^*/2$ and $S_4^*/2$ where the + and - sign in parentheses represent the parity required from the Pauli principle. Extension to higher S_n^* and S_n^*/q are straightforward.

Nuclear Spin Eigenfunction Symmetry of nuclear spin states is obtained by reducing the total character $\chi(G)$ of the nuclear spin states for operation G to irreducible representation $\chi^{(\alpha)}(G)$. The number of each $\chi^{(\alpha)}(G)$ is given by

$$a^{(\alpha)} = \frac{1}{g} \sum_G \chi(G) \chi^{(\alpha)}(G) \quad (40)$$

where g is the dimension of the group (Landau and Lifshitz Vol. III). Just like the original meaning of the word,

character is the part of a subject that does not change by an operation. For nuclei with spin I , we see it is given by $\chi(G) = (2I + 1)^n$ where n is the partition of permutation G . For example, for CH_4 , we have

$$\begin{array}{ccccc} G & I & 8(123) & 3(12)(34) & 6(1234)^* & 6(12)^* \\ \chi(G) & 2^4 & 2^2 & 2^2 & 2^1 & 2^3 \end{array}$$

Thus the symmetry of ψ_n^0 is

$$5A_1 + 3F_2 + E \quad \text{for } S_4^*/2.$$

Note that E^* does not operate on spin and does not affect the counting. Likewise, we have

$$\begin{array}{ll} 3A_1 + B_1 & \text{for } S_2^* \\ 4A_1' + 2E' & \text{for } S_3^* \\ 4A_1 + 2E & \text{for } S_3^*/2. \end{array}$$

and

The relation between the symmetry of the ψ_n^0 and the total nuclear spin quantum number I and spin modifications such as ortho, meta, and para is discussed in Section 3.3.3.

Rotational Eigenfunctions Symmetry of a rotational level is determined by rotational operations corresponding to each permutation-inversion operations listed in Tables 2 and 3. For pure permutation operations, the correspondence is obvious. For a permutation-inversion operation, the correspondence is most directly seen from application of the permutation followed by inversion. Two examples are given in Figure 4.

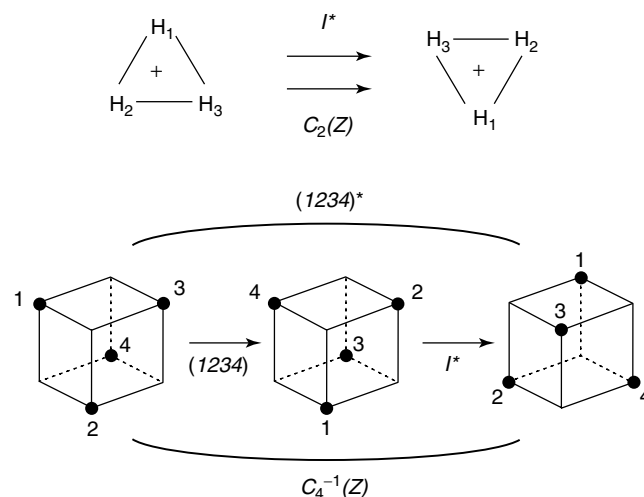


Figure 4 Permutation-inversion operation and corresponding rotational operation for S_3^* molecule, H_3^+ , and $S_4^*/2$ molecule, CH_4 . For methane, black dots represent hydrogen and the central carbon is omitted for simplicity. Note that (1234) and I^* individually are not feasible operations but $(1234)^*$ is feasible.

For asymmetric top molecules with S_2^* symmetry, the symmetry for rotational operations $C_2(X)$, $C_2(Z)$, and $C_2(Y)$ are considered. The energy levels are specified by J_{K_a, K_c} , where K_a and K_c are projections of J onto a - and c -axis, the axis of smallest and largest moment of inertia, respectively. With the choice of the XYZ axes shown in Table 2, c -axis is always Z -axis for a planar molecule but the correspondence between (a, b) axes and (X, Y) axes depends on molecules; for H_2O , $(X, Y) \rightarrow (b, a)$ while for H_2CO , $(X, Y) \rightarrow (a, b)$. The symmetry assignment for rotational levels are

$$A_1(\text{ee}), A_2(\text{oo}), B_1(\text{oe}) \text{ and } B_2(\text{eo}) \text{ for } H_2O$$

$$\text{and } A_1(\text{ee}), A_2(\text{eo}), B_1(\text{oe}) \text{ and } B_2(\text{oo}) \text{ for } H_2CO,$$

where (ee) etc., specify whether K_a and K_c are even or odd.

For symmetric top molecules with S_3^* and $S_3^*/2$ symmetry, the operations $C_3(Z)$ and $C_2(X)$ are considered. The energy levels are specified by J and K and the eigenfunctions are the Wigner function

$$D_{mk}^J(\phi, \theta, \chi) = e^{im\phi} d_{mk}^J(\theta) e^{ik\chi} \quad (41)$$

where ϕ , θ , and χ are Eulerian angles (Landau and Lifshitz Vol. III) and m and k are signed quantum numbers for M and K , the absolute values of projection of J onto a space-fixed z -axis and molecule-fixed Z -axis, respectively. $C_3(Z)$ changes $\chi \rightarrow \chi + \frac{2\pi}{3}$ and $C_2(X)\theta \rightarrow \theta + \pi$ and their eigenvalues (representations) are $e^{2\pi ki/3}$ and $(-1)^J$, respectively. Thus for molecules with $S_3^*/2$ symmetry levels have the following symmetry:

$$A_1 \text{ for even } J \text{ and } A_2 \text{ for odd } J \quad \text{for } K = 0$$

$$A_1 \text{ and } A_2 \quad \text{for } K = 3n(n \neq 0)$$

$$\text{and } E \quad \text{for } K \neq 3n.$$

For molecules with S_3^* symmetry, in which I^* operation is feasible, we need to consider $C_2(Z)$ operation also. We see rotational levels have the following symmetry:

$$A_1' \text{ for even } J \text{ and } A_2' \text{ for odd } J \quad \text{for } K = 0$$

$$A_1' \text{ and } A_2' \quad \text{for } K = 6n(n \neq 0)$$

$$A_1'' \text{ and } A_2'' \quad \text{for } K = 6n \pm 3$$

$$E' \quad \text{for } K = 6n \pm 2$$

$$\text{and } E'' \quad \text{for } K = 6n \pm 1.$$

It is shown below that some of these levels do not satisfy the overall symmetry required by the Pauli principle and thus are not allowed.

For spherical top molecules with $S_4^*/2$ symmetry, rotational operations C_3 , C_2 , and C_4 are considered. Unlike the

previous two cases, there are no special axes and any axis can be used. We take the space-fixed z -axis, which specifies Eulerian angle φ and calculate characters using

$$\chi^{(J)}(\varphi) = \sum_{m=-J}^{m=J} e^{im\varphi} = \frac{\sin(J+1/2)\varphi}{\sin(\varphi/2)} \quad (42)$$

where φ is $2\pi/3$, π , and $\pi/2$ for C_3 , C_2 , and C_4 , respectively (note that $\chi^{(J)}(\varphi)$ does not depend on the sign of φ) (Landau and Lifshitz Vol. III). Decomposing $\chi^{(J)}(\varphi)$ using equation (40) we have

$$A_1 \quad \text{for } J = 0$$

$$F_1 \quad \text{for } J = 1$$

$$E + F_2 \quad \text{for } J = 2$$

$$A_2 + F_1 + F_2 \quad \text{for } J = 3$$

$$\text{and } A_1 + E + F_1 + F_2 \quad \text{for } J = 4 \text{ etc.}$$

Syntheses We now combine the rotational eigenfunction with symmetry Γ_{rot} and the nuclear spin eigenfunction with symmetry Γ_{nuc} such that their product gives symmetry of the total eigenfunction Γ_{total} , which satisfies the Pauli principle, that is, $\Gamma_{\text{rot}} \times \Gamma_{\text{nuc}} \supset \Gamma_{\text{total}}$. The combinations are listed in Table 4. For representations of order 1, the multiplication is obvious. For those of order 2,

Table 4 Combinations of rotational and nuclear spin eigenfunctions which give total eigenfunctions satisfying the Pauli principle.

Symmetry	Γ_{rot}	Γ_{nuc}	Γ_{total}
S_2^*	B_1, B_2	$3A_1$ (ortho)	B_1, B_2
	A_1, A_2	B_1 (para)	
S_3^*	A_2', A_2''	$4A_1'$ (ortho)	A_2', A_2''
	E', E''	$2E'$ (para)	
$S_2^*/2$	$A(-), B(+)$	$3A$ (ortho) $+B$ (para)	$A(-), B(+)$
	$A(+), B(-)$	Forbidden	
$S_3^*/2$	$A_1(-), A_2(+)$	$4A_1$ (ortho)	
	$E(\pm)$ $A_1(+), A_2(-)$	$2E$ (para) Forbidden	$A_1(-), A_2(+)$
$S_4^*/2$	$A_1(-), A_2(+)$	$5A_1$ (meta)	
	$F_1(+), F_2(-)$ $E(\pm)$ $A_1(+), A_2(-),$ $F_1(-), F_2(+)$	$3F_2$ (ortho) E (para) Forbidden	$A_1(-), A_2(+)$

we have $E \times E = A_1 + A_2 + E$ by multiplying characters and decomposing the results to irreducible representations. Likewise, we have $F_1 \times F_1 = F_2 \times F_2 = A_1 + E + F_1 + F_2$, and $F_1 \times F_2 = A_2 + E + F_1 + F_2$.

For S_2^* , all levels are allowed but some levels are forbidden for S_3^* . For example, for H_3^+ with S_3^* symmetry, levels with symmetry A_1' and A_1'' are forbidden, that is, even J levels with $K = 0$, and the A_1' component of $K = 6n$ ($n \neq 0$) doublet levels and the A_1'' component of the $K = 6n + 3$ doublet levels.

We discuss the parity and spin modifications (ortho, para, etc.) in the next two sections.

3.3.2 Parity of Rotational Levels

Rigorous and Nearly Rigorous Symmetry We started our discussion of symmetry by counting out rigorous symmetry operations in Section 3.1. Out of the six operations, three are important for molecular spectroscopy, that is, 1(c) rotation of space, 2(d) inversion of space, and 3 permutation of identical particles; they lead to the rigorous quantum number F (for $F=J+I$), parity, and the rigorous symmetry of the total eigenfunction Γ_{total} , respectively. In contrast, quantum numbers J and I and symmetry Γ_{rot} and Γ_{nuc} are not rigorous although they are very nearly rigorous because of the smallness of the mixing term H_{rn} (Section 2.3.3).

The parity is useful for rigorous discussions of the intramolecular interaction, selection rules, Stark and Zeeman effects, etc., and even collisions. Just as all atomic levels have unique parity, levels of most simple molecules have unique parity. And yet parity of polyatomic molecules has not been discussed in textbooks of molecular spectroscopy. Landau and Lifshitz (1981) is the only textbook that discusses parity extensively. Here the use of parity in energy-level diagrams is advocated. Use of the total nuclear spin I , to be discussed in the next section, is also advocated in addition to or in place of the Placzek symbol. Scientists in other fields understand parity and I but the Placzek symbol, albeit useful as shorthand, is a local language familiar only to molecular spectroscopists.

Assignment of Parity For discussing parity, molecules are classified into three categories (Oka 1973a): molecules (I) for which the symmetry group includes the inversion operation I^* like S_2^* and S_3^* ; molecules (II) for which the group does not include I^* but includes permutation–inversion operations like $S_3^*/2$ and $S_4^*/2$; and molecules (III) for which the group does not include sense reversing operations at all. The molecules (III) have stereoisomers and the discussion of parity is irrelevant since the inversion operation takes a molecule into its enantiomer that cannot be overlapped with the original molecule.

Molecules (I) comprise all linear and planar molecules. The assignment of parity for this class of molecules is straightforward and is given in Herzberg (1989); the symmetry with respect to I^* gives the parity. The I^* operation ($X \rightarrow -X, Y \rightarrow -Y, Z \rightarrow -Z$) is equivalent to a plane reflection of vibronic variables $\sigma_{XY}, (Z \rightarrow -Z)$ and π rotation of the molecular frame, $C_2(Z)$ ($X \rightarrow -X, Y \rightarrow -Y$). Therefore, the parity of a rotational level is determined by whether the angular momentum quantum number along the axis perpendicular to the plane of reflection is even or odd. Thus for linear molecules, planar symmetric top molecules, and planar asymmetric top molecules, the parity is given by $(-1)^J, (-1)^K$, and $(-1)^{Kc}$, respectively. For tunneling nonplanar molecules like NH_3 and NH_2D with umbrella motion, we can assign the parity by simply taking the product of the parities given above and the symmetry of the split levels by the tunneling, which is even for the lower level and odd for the upper level. Almost all astrophysically important molecules such as $H_2, CO, H_3^+, HCO^+, HCN, H_2O, H_2CO, NH_3, H_3O^+$ and many more belong to this category. Their levels are all nondegenerate with single parity.^h

For molecules (II), the discussion of parity is interwoven with that of permutations as we have seen in Section 3.3.1. While for molecules (I) the parity information is already included in Γ_{total} given by the Placzek symbols, for molecules (II) it is additional information. Using character tables given in Table 3 and the results of synthesis in Table 4, we can assign the parity to levels of $S_3^*/2$ and $S_4^*/2$ molecules. For $S_3^*/2$ molecules, the parity for $K = 0$ levels is $(-1)^{J+1}$. $K = 3n$ ($n \neq 0$) levels are split into A_1 and A_2 components (Oka 1967) with parity $-$ and $+$, respectively. Those levels combine with ortho-nuclear spin state ($I = 3/2$). Levels with $K \neq 3n$ are doubly degenerate and have double parity (\pm) and combine para-spin state ($I = 1/2$). For $S_4^*/2$ molecules CH_4 , the assignments are shown in Figure 5.

Application Together with the total angular momentum F , parity is useful for obtaining rigorous selection rules. An intramolecular interaction $\langle \alpha | H | \beta \rangle$ occurs only between two levels α and β of the same parity and F . For example, the off-diagonal spin-rotation interaction H_{rn} , discussed in the next section, mixes ortho and para levels of H_2O or H_2CO only between two levels with ΔK_c even and $\Delta F = 0$. For $S_3^*/2$ molecules like PH_3 or CH_3F , the mixing occurs within the set (A_1 and E^-) and (A_2 and E^+) but not across. The mixing splits E^+ and E^- levels, thus lifting the degeneracy of E^\pm levels, although the splitting is extremely small. Likewise for $S_4^*/2$ molecules like CH_4 the mixing occurs within the sets (A_1, F_2, E^-) and (A_2, F_1, E^+) but not across the sets. Those results will be used in the next section on the stability of spin modifications.

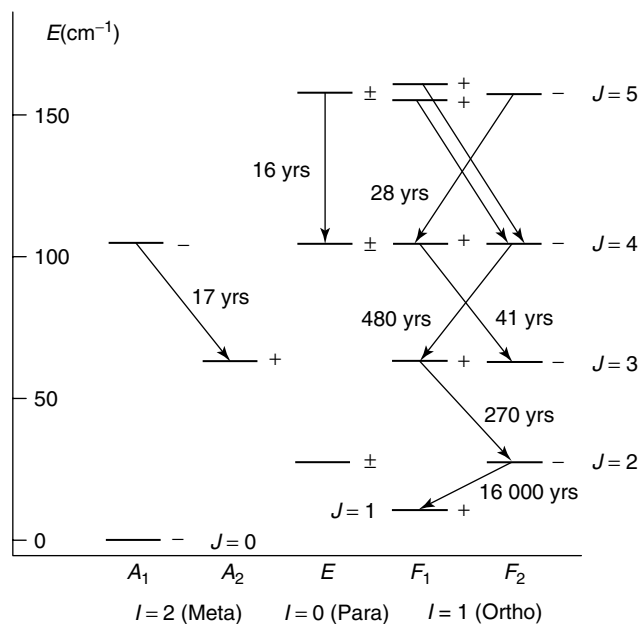


Figure 5 Rotational energy levels and their symmetry for CH_4 with spontaneous emission times. The centrifugal splitting of the highest F_1 level is magnified for clarity.

A mixing of levels by a static electric field and a transition due to an oscillating electric field due to matrix element $\langle \alpha | \mu_e | \beta \rangle$ occurs between two levels with opposite parity, whereas a mixing by magnetic field due to $\langle \alpha | \mu_m | \beta \rangle$ occurs between two levels with the same parity. For this reason, a molecular Zeeman effect for $J \neq 0$ always shows first-order effect linear to the field, whereas the Stark effect is first order only for levels with double parity. For $S_3^*/2$ molecules, the splittings of A_1 and A_2 levels with $K = 3n$ are usually small; their Stark effect starts out as second order but changes to first order for relatively weak electric fields. Rotational transitions and Stark effects exist even for molecules that are usually considered to be nonpolar, such as CH_4 and H_3^+ , due to a breakdown of symmetry by centrifugal distortion. This problem is discussed in Section 3.3.4.

The parity is used also for discussing intermolecular interactions. A rotational transition caused by weak, long-range interactions obeys approximate selection rules (Oka 1973b). In general, if a collision process between molecules 1 and 2 without accompanying spontaneous emission is considered, there exists a rigorous parity relation

$$P_1 P_2 (-1)^L = P'_1 P'_2 (-1)^{L'} \quad (43)$$

where P_1 and P_2 are the parities of the levels of colliding molecules 1 and 2 and L is the angular momentum of relative motion before the collision and P'_1 , P'_2 , and L' are those after the collision. A knowledge of parity is of use

for other molecular interactions such as photodissociation or even chemical reactions if details of the interactions are to be studied. Finally, it is of interest to ask whether *absolute* parity means anything. If molecules are left in an environment with very low temperatures long enough, eventually they will all be in the lowest rotational level. The parity of the lowest level is + for H_2 , CO , HCN , CH^+ , H_2O , etc., whereas it is - for H_3^+ , NH_3 , CH_4 , H_3O^+ , CH_3OH , etc.

3.3.3 Nuclear Spin Modifications

Ortho, Meta, Para The total nuclear spin quantum number I for the vector sum of kinetically equivalent nuclei, $I = \sum_n I_n$ is a robust quantum number that does not change easily because of the extreme weakness of the nuclear magnetic interaction. This was initially conjectured by Dennison to explain the observed enigmatic temperature dependence of the specific heat of H_2 gas (see Tomonaga 1997) and confirmed clearly by successful preparation in 1929 of pure para- H_2 by Bonhoeffer and Harteck. It is now well established that conversion between ortho ($I = 1$) and para ($I = 0$) spin modifications not only of H_2 but also other molecules containing two protons, such as H_2O , H_2CO , are almost rigorously forbidden in spectroscopy (Herzberg 1989) and in collisions (Oka 1973b). The conversion is so slow that for studying their thermalization in interstellar space, the two spin species may be regarded as independent molecules. This applies to the ortho ($I = 3/2$) and para ($I = 1/2$) species of three proton molecules such as NH_3 , CH_3F , etc., and the ortho ($I = 1$), meta ($I = 2$), and para ($I = 0$) species of four-proton molecules such as CH_4 .

The terms ortho and para were initially introduced for the He spectrum empiricallyⁱ and theoretically explained by Heisenberg for the electron species in the atom. Heisenberg used the terms also for protons in H_2 .^j Maue introduced ortho, meta, and para for CH_4 in the order of their statistical weights 9:5:2, which gives their relative population at high temperature and this convention is followed for other molecules. Thus for deuterium, $I = 2$ and $I = 0$ (symmetric with weight 6) are called *ortho*, while $I = 1$ (antisymmetric with weight 3) is called *para*.

Angular Momentum Algebra Symmetry of nuclear spin modifications can also be discussed by using irreducible representations of a rotation group using the almighty formula for addition of angular momenta,

$$D_{I_1} \times D_{I_2} = D_{I_1+I_2} + D_{I_1+I_2-1} + \cdots + D_{|I_1-I_2|} \quad (44)$$

Table 5 Representations and statistical weights of nuclear spin modifications.

n	Examples	Rotation group	PI group	l (ortho)	l (meta)	l (para)	Weight
2	H ₂ , H ₂ O	$D_1 + D_0$	$3A + B$	1		0	3:1
3	NH ₃ , CH ₃ F	$D_{3/2} + 2D_{1/2}$	$4A_1 + 2E$	3/2		1/2	4:4
4	CH ₄ , NH ₄ ⁺	$D_2 + 3D_1 + 2D_0$	$5A_1 + 3F_2 + E$	1	2	0	9:5:2
5	CH ₅ ⁺ , H ₅ ⁺	$D_{5/2} + 4D_{3/2} + 5D_{1/2}$	$6A_1 + 4G_1 + 2H_1$	3/2	1/2	5/2	16:10:6

Table 6

E	8C ₃	3C ₂	6S ₄	6σ _v	
$\chi(M_I = 2)$	1	1	1	1	1
$\chi(M_I = 1)$	4	1	0	0	0
$\chi(M_I = 0)$	6	0	2	0	2

For spin $I = 1/2$, we have a general formula (Section 63, Landau and Lifshitz Vol. III),

$$\left(D_{\frac{1}{2}}\right)^n = \sum_{I=\frac{n}{2}}^{0, \frac{1}{2}} \frac{(2I+1)n!}{\left(\frac{n}{2}-I\right)!\left(\frac{n}{2}+I+1\right)!} D_I \quad (45)$$

where the first and the second index above \sum apply for even and odd n , respectively.

Results for $n = 2-5$ are in Table 5. Symmetry using the permutation–inversion group is also given for comparison. Note that the dimension and frequencies of a representation are swapped between the rotation group and the permutation–inversion group. Table 5 can be readily extended to molecules with larger numbers of protons although we run out of the ortho, meta, and para nomenclature for more than 5 protons.

The symmetry of spin state I using the permutation–inversion group is obvious from Table 5 but it can be derived independently using the point group operations. For example, for a four-proton system of CH₄ where we have $I = 2, 1$, and 0 with $M_I = I, I-1, \dots, -I$, their characters are given in Table 6.

Those characters can be obtained by considering each M_I as a sum of spin pointing up (α ; $M_I = 1/2$) and down (β ; $M_I = -1/2$) and counting out the number of arrangement of α and β , which leave the operations invariant (Landau and Lifshitz Vol. III). The characters for $I = 2, 1$, and 0 are obtained as given in Table 7.

Table 7

$\chi(I = 2) = \chi(M_I = 2) \rightarrow A_1$
$\chi(I = 1) = \chi(M_I = 1) - \chi(M_I = 2) \rightarrow F_2$
$\chi(I = 0) = \chi(M_I = 0) - \chi(M_I = 1) \rightarrow E$

This method can be readily extended for nuclei with spin higher than $1/2$. Thus, for example, for CD₄, by using arrows pointing three different directions, up, horizontal, and down, we can calculate characters for each I and obtain their symmetry, $\chi(I = 4) \rightarrow A_1$, $\chi(I = 3) \rightarrow F_2$, $\chi(I = 2) \rightarrow A_1 + E + F_2$, $\chi(I = 1) \rightarrow F_1 + F_2$, and $\chi(I = 0) \rightarrow A_1 + E$. See Hougen (1976) for individual eigenfunctions.

The use of angular momentum algebra to specify spin modifications is useful for discussing spin selection rules in chemical reactions (Oka 2004).

Transitions between Spin Modifications Since the spin modifications ortho, para, etc., are not rigorous symmetry, transitions between them are allowed albeit extremely weakly. Even the spontaneous emission of H₂, $J = 1$ (ortho) $\rightarrow J = 0$ (para) is “allowed” although its lifetime is much longer than the lifetime of the Universe (Raich and Good 1964).^j Since the mixing of eigenfunctions is given by $\varepsilon = \langle RI | H_m | R'I' \rangle / (E_R - E_{R'})$, the mixing is much larger for spherical top molecules where rotational levels with the same J but different I are nearly degenerate except for the small splitting due to tensorial centrifugal distortion. Ozier *et al.* (1970) observed ortho ($I = 1$) to para ($I = 0$) transition of CH₄ in the $J = 2$ manifold by magnetically shifting a component of Zeeman sensitive $I = 1$ levels to less-sensitive $I = 0$ levels to close the gap of 7.2 MHz. For a heavy spherical top molecule like SF₆, the centrifugal splitting is so minute that different I states are badly mixed and many transitions between them are observed for free molecules (Bordé *et al.* 1980).

For ordinary molecules, however, since $W_{\text{rot}} \sim 10 \text{ cm}^{-1}$ and $W_{I,J} \sim W_{I,I} \sim 3 \text{ kHz}$, the mixing is on the order of $\varepsilon \sim 10^{-8}$ and the smallness of the number explains the stability of spin modifications even in collisions as discussed below.

Conversion of Spin Modifications by Collision Curl *et al.* (1967) were the first to develop a theory for molecular spin conversion of polyatomic molecules by collisions. On the basis of Wigner’s idea in Section 3.1.3, mixing terms for nuclear spin states are those that are invariant for exchange of both Cartesian *and* nuclear spin coordinates but are not invariant for exchange of only Cartesian *or* nuclear spin coordinates. Thus, for example, for S_2^* molecules H₂O and

H₂CO, the proper terms are

$$\hat{H}'_{I,J} = M_{XZ}(I_{1X} - I_{2X})J_Z + M_{ZX}(I_{1Z} - I_{2Z})J_X + Tr. \quad (46)$$

and

$$\hat{H}'_{I,I} = N_{XZ}(I_{1X}I_{2Z} - I_{1Z}I_{2X}) + Tr. \quad (47)$$

where *Tr.* indicates transpose, i.e., $J_Z(I_{1X} - I_{2X})$ for $(I_{1X} - I_{2X})J_Z$, etc. The coordinate *X, Y, Z* is chosen as in Table 2. Note that $M_{XZ} \neq M_{ZX}$. Those terms are essentially the same as given by Curl *et al.* (1967) albeit a little more complete. There are other terms like $(I_{1\alpha} + I_{2\alpha})J_\beta$, $I_{1\alpha}I_{2\alpha}$, $I_{1\alpha}I_{2\beta} + I_{1\beta}I_{2\alpha}$ ($\alpha, \beta = X, Y, Z$), etc., but they are diagonal in *I* and, although they contribute to hyperfine structure, are irrelevant for conversion of spin modifications. The prime sign on $\hat{H}'_{I,J}$ and $\hat{H}'_{I,I}$ indicate terms off diagonal in *I*.

Similarly, the mixing terms for $S_3^*/2$ molecule CH₃F are

$$\begin{aligned} \hat{H}'_{I,J} = & M_{XZ}[(2I_{3X} - I_{1X} - I_{2X})J_Z + \sqrt{3}(I_{1Y} - I_{2Y})J_Z] \\ & + M_{ZX}[-(2I_{3Z} - I_{1Z} - I_{2Z})J_Y + \sqrt{3}(I_{1Z} - I_{2Z})J_X] \\ & + M_{XY}\{[(2I_{3X} - I_{1X} - I_{2X}) - \sqrt{3}(I_{1Y} - I_{2Y})]J_X \\ & - [(2I_{3Y} - I_{1Y} - I_{2Y}) + \sqrt{3}(I_{1X} - I_{2X})]J_Y\} + Tr. \end{aligned} \quad (48)$$

$$\begin{aligned} \hat{H}'_{I,I} = & N_{ZX}^+[2(I_{1Z}I_{2X} + I_{2Z}I_{1X}) - (I_{1Z} + I_{2Z})I_{3X} \\ & - I_{3Z}(I_{1X} + I_{2X}) - \sqrt{3}(I_{1Z} - I_{2Z})I_{3Y} \\ & - \sqrt{3}I_{3Z}(I_{1Y} - I_{2Y})] + N_{ZX}^-[2(I_{1Z}I_{2Y} - I_{2Z}I_{1Y}) \\ & + (I_{1Z} - I_{2Z})I_{3Y} - I_{3Z}(I_{1Y} - I_{1X}) \\ & - \sqrt{3}(I_{1Z} + I_{2Z})I_{3X} + \sqrt{3}I_{3Z}(I_{1X} + I_{2Y})] \\ & + N_{XY}[2(I_{1X}I_{2X} - I_{1Y}I_{2Y}) - (I_{2X}I_{3X} + I_{3X}I_{1X} \\ & - I_{2Y}I_{3Y} - I_{3Y}I_{1Y}) - \sqrt{3}(I_{2X}I_{3Y} - I_{3Y}I_{1X} \\ & + I_{2Y}I_{3X} - I_{3X}I_{1Y})] \end{aligned} \quad (49)$$

Curl *et al.* noted that there often exist accidental near degeneracies between ortho and para levels on the order of $E_R - E_{R'} \sim 0.1 \text{ cm}^{-1}$. For those levels $\varepsilon \sim 10^{-6}$ and for each collision there is a probability of $\varepsilon^2 \sim 10^{-12}$ to convert ortho \leftrightarrow para, in other words, the probability approaches 1 after 10^{12} collisions. Thus, for collision rate constant of $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and pressure of $\sim 1 \text{ torr}$ ($n \sim 3.5 \times 10^{16} \text{ cm}^{-3}$) it takes several hours for conversion and the conversion funnels through such near-degenerate levels.

Experimental measurements of the ortho – para conversion rate have been pioneered and developed by Chapovsky. He used the technique of light-induced drift

developed in the former Soviet Union to create a non-thermal distribution in the ortho – para ratio and measured the recovery directly from the temporal variation of spectral intensities. With many collaborators, Chapovsky obtained the ortho – para conversion rate of $(0.31 \pm 0.03) \times 10^{-3} \text{ s}^{-1} \text{ torr}^{-1}$ for ¹²CH₃F and $(14 \pm 1) \times 10^{-3} \text{ s}^{-1} \text{ torr}^{-1}$ for ¹³CH₃F. Both species have conversion coefficient $M_{\alpha\beta}$ and $N_{\alpha\beta}$ on the order of a few kilohertz and the large difference in conversion rate is simply due to a difference of near degeneracy between the two isotopic species. Readers are referred to Chapovsky and Hermans (1999) for history, experiments, and theory of the field. Conversion rate in CH₃F is considerably faster than that for H₂O or H₂CO because of the first-order Stark shift of levels and resultant level crossings during collisions.

The recent experiment by Takagi and colleagues (Sun *et al.* 2005) of separating the A_g ($I = 2, 0$), B_{1g} , B_{2u} , and B_{3u} ($I = 1$) spin species of ethylene and measuring their conversion rate is noteworthy. The nomenclature of ortho, para, etc., runs out and the spin species are simply represented by symmetry. Their experiment clearly showed that the conversion $B_{2u} \leftrightarrow B_{3u}$, which poses the same parity, occurs in $\sim 10 \text{ min}$ at the pressure of about 1 torr but $B_{2u} \leftrightarrow A_g$ with opposite parity does not occur.

Although at such low pressure, the rate of conversion is proportional to pressure, the proportionality does not apply for much higher pressure because of the uncertainty broadening of the energy levels, which effectively reduces the energy-level separations (Chapovsky and Hermans 1999).

In interstellar space where the density of molecules is very low ($\sim 10^4 \text{ cm}^{-3}$), the time of ortho – para conversion is comparable to the time of star formation. Thus the spin modification may retain the memory of chemistry at the early stage of molecular cloud formation. Such memory, however, is interrupted by chemical reactions, especially through proton exchange reactions with H⁺ and H₃⁺ that need to be considered in order to derive the correct memory. Such reactions were considered with respect to symmetry effect by Quack (1977).

Forbidden Rotational Transitions “Forbidden transitions” mean transitions that do not obey ordinary dipole selection rules. If we consider sufficiently high-order interactions, both time independent and time dependent, no transition in a molecule is strictly forbidden. As the experimental techniques develop, we can study more forbidden transitions.

Symmetry and Orders of Magnitude The electric dipole selection rules for rotational transitions of symmetric top molecules are $\Delta J(\Delta M) = \pm 1, 0$, $\Delta K = 0$, $\Delta I = 0$ (ortho \leftrightarrow ortho, para \leftrightarrow para, etc.), and parity $+$ \leftrightarrow $-$.

22 Orders of Magnitude and Symmetry in Molecular Spectroscopy

Out of these rules, $\Delta K = 0$ is the weakest rule since it is based on geometrical symmetry of equilibrium structure and not on rigorous symmetry operations that lead to the rest of the rules. If the more rigorous symmetry operations of the nuclear permutation is used, the rule should be $\Delta k = 3n$ for S_3^* or $S_3^*/2$ symmetric tops since

$$\begin{aligned} \langle Jk|\mu|J'k'\rangle &= \langle Jk|(123)^{-1}(123)\mu(123)^{-1}(123)|J'k'\rangle \\ &= e^{2\pi i(k'-k)/3} \langle Jk|\mu|J'k'\rangle \end{aligned} \quad (50)$$

The $\Delta k = \pm 3$ transitions are much weaker than the ordinary $\Delta K = 0$ transitions but are still sufficiently strong to be observable by conventional microwave spectrometers (Chu and Oka 1974). For decades, microwave spectroscopists had been limited to the $\Delta K = 0$ transitions and hence only one rotational constant B had been measured, but the $\Delta k = \pm 3$ transitions have allowed the measurement of the other rotational constant A or C .

The breakdown of geometrical symmetry is caused by centrifugal distortion due to rotation around an axis perpendicular to the C_3 axis. Applying the general order of magnitude argument in Section 2.3.1 for vibrational and rotational dependence of any physical quantity f , we find that the coefficient of the rotation-induced electric dipole moment is on the order of $\kappa^4 \mu_e \sim 10^{-4}$ D. Thus for $J \sim 10$, the rotation-induced dipole moment is on the order of $\sim 10^{-2}$ D and its rotation spectrum is $\sim 10^4$ times weaker than ordinary $\Delta K = 0$ spectrum of polar molecules. $\Delta k = \pm 3$ spectra of this magnitude were observed for PH_3 , PD_3 , and AsH_3 (Chu and Oka 1974).

Rotational spectra of tetrahedral molecules induced by the same mechanism have been observed for CH_4 , SiH_4 and GeH_4 . Their $\Delta J = 1$ transitions were observed in the far infrared using high pressure (0.75–1.6 atm) and long path-length cell of over 100 m by Ozier and colleagues and $\Delta J = 0$ transitions were observed in the microwave and in the radiofrequency, the latter using double resonance (Curl 1973). Readers are referred to Oka (1976) for more information on these and other experiments.

Watson's Theory Molecules with more than two equivalent nuclei have high symmetry and accompanying degeneracies but various intramolecular interactions spontaneously break down the symmetry and degeneracies. The Jahn–Teller effect in degenerate electronic states and ℓ -doubling in degenerate vibrational states are well-known examples. Centrifugal distortion of molecules also breaks down symmetry of the molecular configuration and induces spectra that are not expected from the equilibrium structure. Presence of such an effect was initially considered for $\Delta k = \pm 3$ spontaneous emission of interstellar NH_3 (Oka *et al.* 1971). Watson (1971) formulated the general

theory in which it was shown that the forbidden rotational transitions exist for all common highly symmetric molecules except those that have a center of symmetry. He showed that the forbidden spectrum results from intensity borrowing from two ordinary dipole-allowed transitions (i) vibration–rotation transitions and (ii) rotational transitions. The first applies to all molecules and is more general, whereas the second applies only to polar molecules like NH_3 , PH_3 , etc.

Since the beautiful general formulation of Watson may not be easy to follow, the result for the simplest case of H_3^+ is derived here using elementary perturbation theory. The first two terms of the rotational Hamiltonian

$$\hat{H}_{\text{rot}} = \frac{\hbar^2}{2} \left[\frac{J_X^2}{I_{XX}} + \frac{J_Y^2}{I_{YY}} + \frac{J_Z^2}{I_{ZZ}} \right] \quad (51)$$

contains the symmetry breaking term

$$\hat{H}_{\text{S.B.}} = \frac{a\hbar^2}{4\pi I^2} \sqrt{\frac{h}{cv_2}} q_x (J_X^2 - J_Y^2) = 2hc \sqrt{\frac{B^3}{v_2}} q_x (J_X^2 - J_Y^2) \quad (52)$$

where q_x is the dimensionless normal coordinate for the component of the v_2 degenerate vibration symmetric with respect to X . $\hat{H}_{\text{S.B.}}$ is derived by expanding I_{XX} and I_{YY} in H_{rot} into normal coordinate Q_x , $I_{\alpha\alpha} \sim I_{\alpha\alpha}^e + a_x^{\alpha\alpha} Q_x$ ($\alpha = X, Y$) and using $a_x^{YY} = -a_x^{XX} \equiv a = \sqrt{2I}$ and $Q_x = \frac{1}{2\pi} \sqrt{\frac{h}{cv_2}} q_x$ (Oka 1967). We note that $\hat{H}_{\text{S.B.}}$ mixes the ground vibrational state $(v, \ell) = (0, 0)$ and $(1, \pm 1)$ state and rotational level (J, k) with $(J, k \pm 2)$. The spontaneous emission $(J, k) \rightarrow (J, k + 3)$ gains intensity from mixing of $(0, 0, J, k)$ and $(1, -1, J, k + 2)$ and borrowing intensity from the allowed $(1, -1, J, k + 2) \rightarrow (0, 0, J, k + 3)$ transition and mixing of $(0, 0, J, k + 3)$ and $(1, 1, J, k + 1)$ and borrowing intensity from the $(1, 1, J, k + 1) \rightarrow (0, 0, J, k)$ transition. Using matrix elements $\langle 1, 1|q_x|0, 0\rangle = 1/2$ and

$$\begin{aligned} \langle J, k|J_X^2 - J_Y^2|J, k + 2\rangle \\ = \frac{1}{2} [(J - k)(J - k - 1)(J + k + 1)(J + k + 2)]^{\frac{1}{2}} \text{ etc.}, \end{aligned} \quad (53)$$

and using Hönl–London factors for the allowed transitions, we obtain the intensity of $(J, k) \rightarrow (J, k + 3)$ transition as

$$\begin{aligned} S[(J, k) \rightarrow (J, k + 3)] &= \frac{1}{4} (\theta_x^{xx})^2 (J - k)(J - k - 1) \\ &\quad \times (J - k - 2)(J + k - 1) \\ &\quad \times (J + k + 2)(J + k + 3) \\ &\quad (2J + 1)/J(J + 1) \end{aligned} \quad (54)$$

where the Watson coefficient is given as

$$\theta_x^{xx} = 2 \left(\frac{B}{\nu_2} \right)^{\frac{3}{2}} \frac{\partial \mu}{\partial q_2} \quad (55)$$

in terms of the vibrational transition moment of the ν_2 transition $\partial \mu / \partial q_2$. We can obtain corresponding formula for $(J \pm 1, k) \rightarrow (J, k + 3)$ also. θ_x^{xx} is calculated to be 1.08×10^{-3} D (Pan and Oka 1986). Because of the large rotational constant ($B = 44.05 \text{ cm}^{-1}$), Watson's coefficient of H_3^+ is greater than that of NH_3 and CH_4 by 8 and 50, respectively.

Rotational Spontaneous Emission of Interstellar H_3^+ The forbidden rotational transition was initially considered as a possible mechanism of thermalization of interstellar NH_3 (Oka *et al.* 1971). Interstellar NH_3 is produced in high rovibrational levels by chemical reactions but cools down to a lower level by a succession of dipole-allowed spontaneous emissions $(J, K) \rightarrow (J, K - 1)$ in a minute or so until it reaches the lowest $J = K$ metastable level. The spontaneous emission between the inversion levels is much slower and takes a few months. It was initially thought that dipole forbidden spontaneous emission from the metastable level to lower level needs to invoke the molecular octopole moment (because $\Delta k = 3$) and thus takes longer than the lifetime of the Universe. The spontaneous breakdown of symmetry mentioned above showed that the $\Delta k = \pm 3$ dipole transitions due to intensity borrowing are possible. The calculated emission lifetimes are 230 years, 43 years, and 22 years for $(2,2) \rightarrow (1,1)$, $(3,3) \rightarrow (2,0)$ and $(4,4) \rightarrow (3,1)$, respectively. Although they are faster than previously thought by some 10 orders of magnitude, they are still not fast enough to be competitive with collisional relaxation whose time interval is typically a few months at the molecular cloud density of $\sim 10^4 \text{ cm}^{-3}$.

This situation has changed drastically when interstellar H_3^+ was discovered (Geballe and Oka 1996). Since the Einstein coefficient for spontaneous emission is proportional to ν^3 and Watson's coefficient is proportional to $B^{3/2}$, the spontaneous emission time is approximately proportional to the sixth power of the moment of inertia. It is shorter for H_3^+ ($B = 44.05 \text{ cm}^{-1}$) than for NH_3 ($B = 9.94 \text{ cm}^{-1}$) by nearly four orders of magnitude. The spontaneous emission times for H_3^+ are about a month or less. The rotational energy diagram of H_3^+ and spontaneous emission times are given in Figure 6. Even the longest time of 27 days for the $(2,2) \rightarrow (1,1)$ spontaneous emission is competitive with collisions in dense clouds. It is much faster in diffuse clouds with density of $\sim 10^2 \text{ cm}^{-3}$ and create a remarkable nonthermal proportional distribution (negative temperature) between the $(3,3)$ metastable level and the

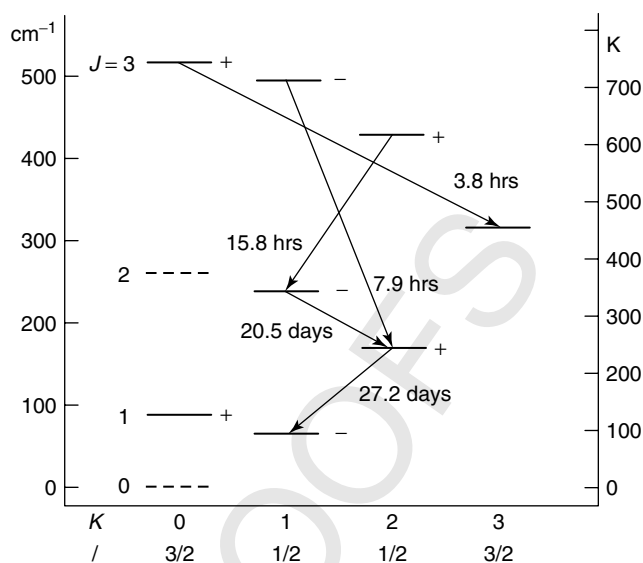


Figure 6 Rotational levels of H_3^+ and their symmetry. Spontaneous emissions are shown by arrows with emission time.

$(2,2)$ unstable level. The competition between the spontaneous emission and collision makes the population of the $(2,2)$ level a sensitive indicator of the cloud density and the population of the $(3,3)$ level, which is 361 K above the lowest $(1,1)$ level, serves as a thermometer. A model calculation of thermalization of interstellar H_3^+ has been worked out (Oka and Epp 2004) and using its result, observations have led to revelations of hitherto unsuspected presence of a vast amount of high temperature ($T \sim 250 \text{ K}$) and low density ($n \sim 100 \text{ cm}^{-3}$) molecular gas near the Galactic center (Oka *et al.* 2005).

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ENDNOTES

^aThis is not the case if SI units are used. In the SI unit system where ϵ_0 and μ_0 are not equal to 1, physical quantities involving c can be written in more than one way. The fine structure constant, for instance, is either $\frac{e^2}{2\epsilon_0 hc}$ or $\frac{e^2 \mu_0 c}{2h}$ or $\frac{e^2}{2h} \sqrt{\frac{\mu_0}{\epsilon_0}}$, that is, c , ϵ_0 , and μ_0 appear and disappear. This is one of several reasons why authors of high-level textbooks dislike using SI units.

^bThe first three volumes of Landau and Lifshitz are quoted many times in this chapter. For those with different

versions, we mention just volumes without published year except for special cases.

^cReaders are referred to Vilenkin (1988) for Lie groups and special functions as their representations.

^dFor a quantum mechanical state involving a half-integer spin, the time reversal operator has to be applied four times to bring the system back to its original state. This is analogous to the fact stated earlier in the previous section that a rotation of 2π changes the sign of the eigenfunction for half-integer spin which comes back to the original state only after a rotation of 4π .

^eUpper limits of the electric dipole moment of the electron 8.6×10^{-19} D and the neutron 3.0×10^{-17} D have been reported.

^fAn upper limit for splitting on the order of $\Delta\nu/\nu \sim 10^{-14}$ has been reported.

^gSee Appendix 1 of Edwards (1984) for a full translation.

^hThe degeneracy of the K quantum number, k and $-k$, for example in H_3^+ , disappears since only $|k > -|k >$ satisfies the Pauli Principle for $k \neq 3n$.

ⁱRunge and Paschen (1896) observed two sets of spectral lines and ascribed the stronger one to helium and weaker one to “parhelium”. Later Bohr recommended to call the stronger one “ortho-helium”.

^jThe citation to Heisenberg’s Nobel Prize in 1932 reads “for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of allotropic forms of hydrogen”, indicating that the ortho–para H_2 was a big issue at the time.

^kThe mixing cannot occur within the $^1\Sigma_g^+$ ground state but can occur with levels with the same parity and F in $^1\Sigma_u^+$ or Π_u excited states and borrow intensities from the allowed $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ transitions, etc.

ABBREVIATIONS AND ACRONYMS

QED Quantum Electrodynamics

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ABSTRACT: Considerations of the order of magnitude and the symmetry of various intramolecular interactions form the foundation of molecular spectroscopy. They are related and they together make molecular spectroscopy transparent and tidy. In this chapter, they are discussed starting from the very fundamental. The order of magnitude has not been discussed in any previous textbooks of molecular spectroscopy. The symmetry has been discussed in many textbooks and discussions here are limited to the rotational and nuclear spin states and its application to forbidden rotational transitions and the stability of nuclear spin modifications (ortho-, para- etc.).

KEYWORDS: molecular spectroscopy; order of magnitude; fine structure constant; Born–Oppenheimer constant; symmetry; permutation–inversion group; parity; molecular rotation; spin modification; forbidden rotational transition

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