

Radiative Transitions

33. Radiative Transition Probabilities

This chapter summarizes the theory of radiative transition probabilities or intensities for rotationally-resolved (high-resolution) molecular spectra. A combined treatment of diatomic, linear, symmetric-top, and asymmetric-top molecules is based on angular momentum relations. Generality and symmetry relations are emphasized. The *energy-intensity* model is founded in a rotating-frame basis-set expansion of the wave functions, Hamiltonians, and transition operators. The intensities of the various rotational branches are calculated from a small number of transition-moment matrix elements, whose relative values can be assumed from the supposed nature of the transition, or inferred by fitting experimental intensities.

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33.1 Overview

33.1.1 Intensity versus Line-Position Spectroscopy

The fact that atoms and molecules absorb and emit radiation with propensities that vary with wavelength is the origin of the field called spectroscopy. The relatively sharp intensity maxima are interpreted as corresponding to transitions between discrete states or energy levels. The frequencies or energies of these transitions are used

as the primary source of information about the internal structure of the atom or molecule. Line positions can be measured with very high precision (1 ppm or better). Excellent calibration standards have been developed. The quality of these experimental data has attracted extensive analytical and theoretical effort. Sophisticated parametrized models have been developed in which the smallest shifts from the expected line positions can be used to identify perturbations or other subtle effects.

For molecules, knowledge of the strengths of these transitions is far less well developed. One reason is that quantitative experimental data on rotationally-resolved absorption cross sections and emission intensities are much rarer and the experiments themselves are much more difficult to calibrate. Few measurements claim a precision better than 1% and agreement within 10% of measurements in different laboratories is typically viewed as good. This situation is undesirable

because most applications of molecular spectroscopy are in fact measurements of intensity. In many cases the strengths of absorptions or emissions are used to infer gas composition, temperature, time evolution, or other environmental conditions. In other examples the actual absorption and emission is the primary interest. Among the most important of these are atmospheric absorption of solar radiation and the greenhouse effect.

33.2 Molecular Wave Functions in the Rotating Frame

33.2.1 Symmetries of the Exact Wave Function

The exact total wave function for any isolated molecule with well-defined energy and total angular momentum can be expressed in a basis-set expansion over configurations with well-defined internal quantum numbers,

$$\begin{aligned} \Phi_{\text{exact}} & \quad (33.1) \\ & = \Phi_{\text{trans}} \sum_{\alpha\beta\gamma\delta\epsilon} C_{\alpha\beta\gamma\delta\epsilon} \Phi_{\text{rot}}^{\alpha} \Phi_{\text{vib}}^{\beta} \Phi_{\text{elec}}^{\gamma} \Phi_{\text{espin}}^{\delta} \Phi_{\text{nspin}}^{\epsilon} . \end{aligned}$$

In principle, the coefficients $C_{\alpha\beta\gamma\delta\epsilon}$ can be found only by diagonalizing the exact Hamiltonian. In practice one attempts to find a sufficiently good approximation, containing only a few terms, with coefficients chosen by diagonalizing an approximate or model Hamiltonian. This is the basis of the energy–intensity model developed in Sect. 33.3. As discussed by *Longuet-Higgins* [33.1] and *Bunker* [33.2], there are only six true symmetries of the exact Hamiltonian of an isolated molecule:

1. translation of the center of mass;
2. permutation of electrons;
3. permutation of identical nuclei;
4. time reversal or momentum reversal;
5. inversion of all particles through the center of mass;
6. rotation about space-fixed axes.

Of these, only the symmetries numbered 5 and 6 give quantum numbers (parity and the total angular momentum F) that are both rigorous and useful spectroscopic labels of the states of the molecule. The other symmetries are convenient for simplifying the description of the molecular wave function, for the evaluation of relations between matrix elements, and for classification of molecular states according to approximate symmetries.

The first symmetry, translation of the center of mass, allows the choice of a coordinate system referenced to the center of mass, and suppression of the portion of the

wave function describing motion through space (as long as the molecule does not dissociate).

Symmetry number 2, exchange of electrons, does not directly provide any labels or quantum numbers, since the Fermi–Dirac statistics of electrons require that all wave functions must be antisymmetric. However, it provides considerable information about the probable electronic states since it controls whether molecular orbitals can be doubly or only singly occupied. For most (low- Z) molecules, each state will have a nearly well-defined value of electron spin: singlet or triplet for example. Admixture of other spin values usually can be treated as a perturbation. These points will be elaborated in Sects. 33.4.4 and 33.7.4.

Permutation of identical nuclei, symmetry number 3, also gives an identical quantum number to all the states of the molecule (± 1 depending on the character of the permutation and on whether nuclei with integral or half-integral spin are being permuted). It supplies little direct information about the energy separations between the states of the molecule. On the other hand, many molecules have identical nuclei in geometrically or dynamically equivalent positions. The existence of spatial symmetry, for nonplanar molecules, is really the same thing as permutational symmetry. Consequently, nuclear permutation, combined with inversion (symmetry number 5), is the basis for naming the states according to the approximate spatial symmetry group of the molecular frame and vibrational motion. These concepts will be explored in Sect. 33.4.3.

Symmetry number 4, time reversal, is both subtle and simple. In the absence of external magnetic fields the Hamiltonian for a molecule will contain only even combinations of angular momentum operators, e.g., $F_{\alpha}F_{\beta}$, $F_{\alpha}L_{\beta}$, or $F_{\alpha}S_{\beta}$. Thus changing the signs of all the angular momenta should result in an equivalent wave function. This will require that matrix elements retain

the same absolute value when the angular quantum numbers are reversed, leading in general to complex conjugation [33.3].

Spatial inversion, symmetry number 5, is always an allowed operation for any molecule, even if it appears to lack internal inversion symmetry. This operation can be considered as a symmetry of the spherically-symmetric laboratory in which the molecule resides. If the molecule is linear, triatomic, rigid with a plane of symmetry, or is nonrigid with accessible vibrational or tunneling modes that correspond to plane reflections, inversion symmetry divides the states of the molecule into two classes, called parities. Perturbations can occur only between states of the same parity. For optical transitions, the change in parity of the states must match the parity of the operator. Otherwise, reflection of the molecule in a plane will interchange inconvertible optical isomers. Such optical isomers are energetically degenerate, so in all cases, inversion through the center of mass remains a valid symmetry of the rotating molecule. However, the separation of the states into two kinds does not provide any selection rules. The two parity classes are perfectly degenerate, thus there is always an allowed level with the correct parity either for perturbations or for optical transitions.

33.2.2 Rotation Matrices

The final symmetry, rotation about the center of mass, restricts the discussion to states with well-defined laboratory angular momentum, and to re-expression of the exact wave function by changing variables from *laboratory* coordinates to *body-fixed* or internal coordinates, and introducing the Euler angles relating these two coordinate systems,

$$\Phi_{\text{exact}}^{F, M_F}(\text{lab}) = \sum_{K_F} \Phi_{\text{rot}}^{F, M_F K_F}(\text{Euler angles}) \times \Phi_{\text{vesn}}^{(F, K_F)}(\text{internal, spins}). \quad (33.2)$$

Here F is the total angular momentum of the molecule, including vibrational, mechanical-rotation, electron-orbital, electron-spin, and nuclear-spin contributions. M_F and K_F are the projections of F in the laboratory and body-fixed frames, respectively. In the majority of cases, the magnitude of nuclear hyperfine interactions is sufficiently small that its influence can be ignored when analyzing wave functions and computing energies. Thus the quantum numbers J , M_J , and K_J , or just J , M , and K can be used.

Explanation is postponed of how the body-fixed frame is to be selected, but for any choice, the wave function for rotation of the entire molecule can be expressed using a rotation matrix [33.4, 5]

$$\Phi_{\text{rot}}^{F, M_F K_F}(\text{Euler angles}) = \left(\frac{(2F+1)}{8\pi^2} \right)^{1/2} D_{M_F K_F}^{*F}(\phi, \theta, \chi). \quad (33.3)$$

For diatomics, Zare [33.5] suggests multiplying by $(2\pi)^{1/2}$ and setting $\chi = 0$. The internal wave function for the vibrational, electronic, electron-spin, and nuclear-spin degrees of freedom [thus the label (vesn)] can be thought of as the partial summation

$$\Phi_{\text{vesn}}^{(F, K_F)}(\text{internal, spins}) = \sum_{\beta\gamma\delta\epsilon} C_{(FK_F)\beta\gamma\delta\epsilon} \Phi_{\text{vib}}^{\beta} \Phi_{\text{elec}}^{\gamma} \Phi_{\text{espin}}^{\delta} \Phi_{\text{nspin}}^{\epsilon}, \quad (33.4)$$

expressed in the internal or rotated coordinate system. Note that the FK_F designation is only a parametric label. The rotational wave function has been absorbed into the rotation matrix.

33.2.3 Transformation of Ordinary Objects into the Rotating Frame

The assumption of rotational symmetry allows re-expression of matrix elements between total wave functions as a sum of matrix elements between internal wave functions. For example, the tensor operator $T^{(L)}$ belonging to the L representation of the rotation group, can be written in the rotating frame as [33.5–8]

$$T_p^{(L)}(\text{lab}) = \sum_q D_{pq}^{*L}(\phi\theta\chi) T_q^{(L)}(\text{body}), \quad (33.5)$$

and can be used to evaluate matrix elements that might represent radiative transitions:

$$\begin{aligned} & \langle \psi^{F', M_F' + p} | T_p^{(L)}(\text{lab}) | \Phi^{F'', M_F''} \rangle \\ &= \left(\frac{(2F''+1)}{(2F'+1)} \right)^{1/2} \langle F'' M_F'', Lp | F' M_F' + p \rangle \\ & \times \sum_{q K_F''} \langle F'' K_F'', Lq | F' K_F' + q \rangle \\ & \times \langle \psi_{\text{vesn}}^{(F', K_F' + q)} | T_q^{(L)}(\text{body}) | \Phi_{\text{vesn}}^{(F'', K_F'')} \rangle, \quad (33.6) \end{aligned}$$

where $\langle F'' M_F'', Lp | F' M_F' + p \rangle$ and $\langle F'' K_F'', Lq | F' K_F' + q \rangle$ are Clebsch–Gordan coefficients that vanish if $|F' - F''| > L$, $|M_F'' + p| > F'$, or $|K_F'' + q| > F''$.

This transformation forms the basis for the derivation of rotational branch strengths (Sect. 33.7.2) and for the

description of electron motions that are weakly coupled to the molecular frame (Sect. 33.7.4).

33.3 The Energy–Intensity Model

33.3.1 States, Levels, and Components

The previous section introduced the concept of representing the wave function of a molecule as a product of five simpler wave functions:

$$\psi \approx \psi_{\text{elec}} \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{espin}} \psi_{\text{nspin}} . \quad (33.7)$$

This construction yields a similar separation of the Hamiltonian,

$$H \approx H_{\text{elec}} + H_{\text{vib}} + H_{\text{rot-fs}} + H_{\text{hf}} , \quad (33.8)$$

and representations of the energies as sums of contributions,

$$E \approx T_e + G_v + F_c(J) , \quad (33.9)$$

and absorption or emission transition strengths as products,

$$I \approx I_{\text{elec}} I_{\text{vib}} I_{\text{rot-fs}} I_{\text{hf}} . \quad (33.10)$$

Whatever theoretical arguments might favor such a separation, the real impetus is the empirical observation that most molecular absorption and emission spectra exhibit recognizable patterns arising from the dissimilar magnitudes of the energies associated with these five degrees of freedom. Separation of the wave function and the Hamiltonian into these four or five contributions facilitates the assignment of molecular spectra, in addition to suggesting models with parameters that can be adjusted to quantitatively represent the observed spectra.

Most states of molecules are dominated by a single set of electronic and vibrational quantum numbers. Electronic states are often well separated. With each electronic state is associated a potential energy surface, the energy at the minimum being labeled T_e . Motion of nuclei within this potential generates various levels corresponding to different vibrational quantum numbers, following regular patterns or progressions in energy, summarized by a small number of parameters called vibrational frequencies. The quantity G_v represents the energy of the the vibrational level above the potential minimum. For each vibrational level, a progression of rotational levels is expected. For linear molecules in electronic states without electronic

angular momentum (i. e., $^1\Sigma$ states) the rotational energies are also reproduced by a few rotational constants.

For more complicated molecules and electronic states, i. e., most cases, there are multiple energetically distinct levels with the same value of J (in addition to the $2J + 1$ orientational degeneracy of each level). These multiple levels all share the same nominal quantum numbers (additional analysis may subdivide them into parity or permutational symmetry types). These sub-levels are called “components” with energies expressed by the notation $F_c(J)$. The quantity N_c , the number of components expected, reflects the assignment of the nature of the vibronic state. For linear molecules there is a limited number of components corresponding to the various orientations of electron spin and orbital angular momentum. For example, a $^2\Pi$ electronic state will have four components for each value of J (except for $J = 1/2$, where there are only two components). For nonlinear molecules the number of components increases with J , proportional to $2J + 1$, corresponding to various possible projections of the total angular momentum onto the tumbling molecular frame.

The conclusion of this analysis is that a basis set be chosen, over which a model rotational and fine-structure Hamiltonian can be expressed. The wave functions then become vectors of numbers. A priori, only the form of the matrix elements and their dependence on J and body–frame projection (K or Ω) are known. Little is known in advance about how strong the interactions are in any given molecule. Thus one tends to write the Hamiltonian with parameters that are to be determined by fitting the observed energy levels.

Similarly, the choice of the basis sets for the upper and lower states specifies the overall form of the matrix of transition moments between the basis functions. The transition can be chosen to be of a simple standard form, for example, parallel or perpendicular, with only one unknown parameter representing the overall strength of the transition. Alternatively, the transition matrix elements can be considered to be independently adjustable, within the symmetry restrictions that are required (time reversal) or assumed (spatial symmetry).

33.3.2 The Basis Set and Matrix Hamiltonian

For linear molecules it is convenient to choose a basis set labeled by the projections of orbital and spin angular momenta in the body–frame coordinate system, represented symbolically by

$$|\Lambda\Sigma; JM\Omega\rangle = \left(\frac{(2J+1)}{8\pi^2}\right)^{1/2} D_{M\Omega}^{*J} |\Lambda\Sigma\rangle, \quad (33.11)$$

where $\Omega = \Lambda + \Sigma$. This is called the Hund’s case (a) basis set, which is an accurate representation in a single term if the body–frame angular momenta are nearly conserved. This is true if the spin-orbit interaction is larger than the separation between rotational levels. Under all circumstances, this basis set facilitates construction of the matrix Hamiltonian and representation of sources of transition probability [33.9].

One parametrization for the spin–rotation Hamiltonian is provided by *Brown et al.* [33.10–12]:

$$\begin{aligned} H_{\text{spin-rot}} &= T_e + G_v + B_v N^2 - D_v N^4 \\ &+ \frac{1}{2} [A_v + A_{D_v} N^2, L_z S_z]_+ \\ &+ (\gamma_v + \gamma_{D_v} N^2) \mathbf{N} \cdot \mathbf{S} \\ &+ \frac{1}{3} [\lambda_v + \lambda_{D_v} N^2, 3S_z^2 - S^2]_+ \\ &+ \eta_v L_z S_z [S_z^2 - \frac{1}{5}(3S^2 - 1)] \\ &- \frac{1}{4} [o_v + o_{D_v} N^2, \Lambda_+^2 S_-^2 + \Lambda_-^2 S_+^2]_+ \\ &+ \frac{1}{4} [p_v + p_{D_v} N^2, \Lambda_+^2 S_- N_- + \Lambda_-^2 S_+ N_+]_+ \\ &+ \frac{1}{4} [q_v + q_{D_v} N^2, \Lambda_+^2 N_-^2 + \Lambda_-^2 N_+^2]_+, \quad (33.12) \end{aligned}$$

where $[x, y]_+$ is the anticommutator $(xy + yx)$, and $\mathbf{N} = \mathbf{J} - \mathbf{S}$. *Zare et al.* [33.13] provide an alternative parametrization, with different interpretations of the *spectroscopic constants* (B, D, A, γ, λ , etc.) because they multiply different symbolic operators. One significant difference is that *Zare et al.* use the “mechanical angular momentum” $\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S}$ as the expansion operator, rather than \mathbf{N} , which might be called the “spinless angular momentum.” These differences mean that care must be taken in attempting to construct simulated spectra from published constants. In spite of much discussion in the literature, there is little theoretical foundation for

preferring one parametrization over another, as long as the observed levels are accurately fit. In a number of cases naive assumptions about the origin of certain types of interactions have been overturned. For example, the spin–spin interaction, represented by the constant λ , is often dominated by level shifts due to off-diagonal spin-orbit perturbations [33.14].

For polyatomic molecules, a suitable basis set for expansion can be chosen to have a similar form [33.8, 15, 16]

$$|l\Lambda\Sigma; JMK\rangle = \left(\frac{(2J+1)}{8\pi^2}\right)^{1/2} D_{MK}^{*J} |l\Lambda\Sigma\rangle, \quad (33.13)$$

where Λ and Σ represent the projections of the electron–orbital (L) and spin (S) angular momenta, and l represents the projection of the vibrational angular momentum (p for degenerate vibrational modes). This is the symmetric top basis set. Generalizing the work of *Watson* [33.17, 18], the parametrized Hamiltonian might be written in a form such as

$$\begin{aligned} H_{\text{rot}} &= \sum h_{\zeta\eta\theta l}^{\alpha\beta\gamma\delta\epsilon} \left\{ (J^2)^\alpha (J_z)^{2\beta} (J_+^{2\gamma} + J_-^{2\gamma}) \right. \\ &\quad \times (\mathbf{J} \cdot \mathbf{p})^\delta (\mathbf{J} \cdot \mathbf{L})^\epsilon (\mathbf{J} \cdot \mathbf{S})^\zeta \\ &\quad \left. \times (\mathbf{p} \cdot \mathbf{L})^\eta (\mathbf{p} \cdot \mathbf{S})^\theta (\mathbf{L} \cdot \mathbf{S})^l \right\}, \quad (33.14) \end{aligned}$$

where the $\{\}$ indicates that an appropriately symmetric combination be constructed with anticommutators.

For both linear and nonlinear molecules, it is convenient to use the Wang transformation [33.19] to combine basis functions with opposite sense of rotation: for diatomics

$$\frac{1}{\sqrt{2}} [|l, \Lambda, \Sigma; J, M, \Omega\rangle \pm |l, -\Lambda, -\Sigma; J, M, -\Omega\rangle]; \quad (33.15)$$

and for polyatomics

$$\frac{1}{\sqrt{2}} [|l, \Lambda, \Sigma; J, M, K\rangle \pm |l, -\Lambda, -\Sigma; J, M, -K\rangle]. \quad (33.16)$$

For diatomic molecules, these combinations can be assigned the parity $\pm(-1)^{J+S+s}$, where $s = 1$ for Σ^- states, and 0 otherwise [33.13, 20]. For symmetric top molecules, each term is to be accompanied by the appropriate hidden nuclear-spin basis function [33.8, 21].

For asymmetric top molecules, the Wang transformation divides the basis functions into four symmetry

classes E^\pm and O^\pm according to the combining sign and whether K is even or odd. The eigenstates are often labeled by two projection quantum numbers called K_{-1} and K_1 . Assuming that $A \geq B \geq C$, the asymmetry parameter

$$\kappa = \frac{(2B - A - C)}{(A - C)} \quad (33.17)$$

ranges from -1 for a prolate symmetric top ($B = C$) to 1 for an oblate symmetric top ($B = A$). A , B , and C are the rotational constants, or reciprocals of the moments of inertia, about the three principal top axes. Each asymmetric top level can be correlated with specific symmetric top levels (i.e., K -values) in the two limits. The prolate limiting K -value is called K_{-1} and the oblate limit is called K_1 (i.e., $\kappa = \pm 1$). Note that the symmetric-top principal axes rotate by 90° during this correlation. The eigenstates are given additional symmetry names (ee, eo, oe, oo) according to whether K_{-1} and K_1 are even or odd. *Papousek and Aliiev* [33.18] discuss the relations between the (E^\pm , O^\pm) and (ee, eo, oe, oo) labeling schemes.

33.3.3 Fitting Experimental Energies

Having chosen a basis set and model Hamiltonian for both the upper and lower levels, the observed transition energies can be used to infer the numerical values of the constants that best fit the spectrum. The following quotation provides a good description of the process:

The calculational procedure logically divides into three steps: (1) The matrix elements of the upper and lower state Hamiltonians are calculated for each J value using initial values of the adjustable molecular constants; (2) both Hamiltonians are numerically diagonalized and the resulting sets of eigenvalues are used to construct a set of calculated line positions; and (3) from a least-squares fit of the calculated to the observed line positions, an improved set of molecular constants is generated. This nonlinear least-squares procedure is repeated until a satisfactory set of molecular constants is obtained.

This quotation is taken from the article by *Zare et al.* [33.13] in which they describe the basis for the LINFIT computer program, one of the first to accomplish direct extraction of constants from diatomic spectral line positions based on numerically diagonalized Hamiltonians.

33.3.4 The Transition Moment Matrix

Diagonalization of the model Hamiltonians for the upper and lower states yields vector wave functions that can be used for calculating matrix elements, especially those needed to evaluate radiative transition probabilities. The wave functions for diatomic molecules have the form

$$\begin{aligned} \psi'_{J'M'e'} &= \sum_{\Lambda'\Sigma'} b'_{\Lambda'\Sigma'} | \Lambda' \Sigma'; J' M' \Omega' \rangle', \\ \Phi''_{J''M''e''} &= \sum_{\Lambda''\Sigma''} a''_{\Lambda''\Sigma''} | \Lambda'' \Sigma''; J'' M'' \Omega'' \rangle''. \end{aligned} \quad (33.18)$$

Section 33.2.3 expresses matrix elements of laboratory-frame operators in terms of matrix elements in the rotating body-fixed frame. Terms of the form

$$\mu_{K'K''} = \langle \psi^{(J'K')} | T_q^{(L)}(\text{body}) | \Phi^{(J''K'')} \rangle \theta(-q) \quad (33.19)$$

need to be evaluated. These terms are multiplied by zero if $K' \neq K'' + q$. In the diatomic basis set these become

$$\mu_{\Lambda'\Sigma'\Lambda''\Sigma''} = \langle \Lambda'\Sigma' | T_q^{(L)}(\text{body}) | \Lambda''\Sigma'' \rangle \theta(-q), \quad (33.20)$$

where $\theta(-q)$ is a phase factor described in Sect. 33.7.2. Only a few of these matrix elements are independent and nonzero. For electric dipole transitions ($L = 1$), time-reversal and inversion-symmetry can be used to establish the relation

$$\mu_{-\Omega' - \Omega''} = \eta(-1)^{\Omega' - \Omega''} \mu_{\Omega' \Omega''}. \quad (33.21)$$

The sign of $\eta = \pm 1$ is determined by the overall character of the electronic transition, and is related to the classification of levels into e - and f -parity types and to the determination of which components are involved in the rotational branches (P , Q , and R). These concepts are elaborated in Sect. 33.4.

33.3.5 Fitting Experimental Intensities

For allowed transitions in linear molecules and symmetric tops, only one independent parameter is normally expected in the transition moment matrix. Thus no additional information is available from fitting the experimental rotational branch strengths (assuming the energy-intensity model is adequate). In diatomic molecules, the intensities of different vibrational bands can be used to infer the internuclear-distance dependence of the electronic transition moment (for example, see *Luque and Crosley* [33.22]).

For forbidden transitions and allowed transitions in asymmetric tops, more than one independent parameter is expected. The intensity of a single given rotational line can be expressed in the form

$$I^{\text{line}} = \left| \sum_{K'K''} \mu_{K'K''} Z_{K'K''}(\text{line}) \right|^2, \quad (33.22)$$

33.4 Selection Rules

33.4.1 Symmetry Types

Selection rules are guidelines for identifying which transitions are expected to be strong and which are expected to be weak. These rules are based on classifying rovibronic levels into labeled symmetry types. Some symmetry distinctions are effectively exact: such as total angular momentum F , or laboratory-inversion parity. Others are approximate, derived from estimates that certain matrix elements are expected to be much larger than others. The most important of these are based on electron spin (for light molecules) and geometrical point-group symmetry (for relatively rigid polyatomics). In actual fact, no transition is completely forbidden. The multipole nature of electromagnetic radiation (electric-dipole, magnetic-dipole, electric-quadrupole, etc.) implies that any change in angular momentum or parity is possible in principle. Practical interest emphasizes identification of the origin of the strongest source of transition probability, and estimation of the strengths of the weak transitions relative to the stronger ones. The result is a collection of *propensity rules* using *selection rules* as tools of estimation.

Basis functions for expansion of the wave functions for the upper and lower states were chosen in Sect. 33.3.2. The first step in the symmetry classification of rovibronic levels consists of identifying various linear combinations of basis functions that block-diagonalize the exact or approximate Hamiltonians. Symmetry-type names are then assigned to these linear combinations based on the value of F or J and knowledge of the symmetry properties of the underlying vibrational and electronic states. Thus each eigenfunction or rovibronic level consists of an expansion over only one of the kinds of linear combination, and the level can be assigned a specific symmetry type.

Similarly, the basis-set expansion leads to a matrix representation of the possible transitions. Spin- and spatial-symmetry arguments establish relationships be-

where $Z_{K'K''}$ (line) can be calculated in advance from the energies (wave functions) and quantum numbers alone, using the formulas in Sect. 33.7.2. Nonlinear least-squares fitting can be used to derive the best intensity parameters [33.23–26], analysis of which can help characterize the nature of the transition, and identify the sources of transition probability.

tween these transition matrix elements, and provide estimates of which are much smaller than the others. Each combination of upper- and lower-state symmetry types results in a specific pattern of rotational branches. The most important patterns are ΔJ even (Q -branches) or odd (P - and R -branches), and intensity alternation for consecutive values of J (nuclear spin statistics).

33.4.2 Rotational Branches and Parity

The symmetry of time or momentum reversal implies that changing the signs of all the angular momenta should result in an equivalent wave function. For example, the phase convention

$$\begin{aligned} & \Phi_{\text{vesn}}^{(F, -K_F)}(\text{internal, spins}) \\ &= (-1)^{-F+K_F} \Phi_{\text{vesn}}^{*(F, K_F)}(\text{internal, -spins}) \end{aligned} \quad (33.23)$$

can be chosen to establish that the relative phases of matrix elements of the Hamiltonian can be taken as

$$\begin{aligned} & \left\langle D_{M_F - K'_F}^{*F} \Phi_{\text{vesn}}^{(F, -K'_F)} \middle| H \middle| D_{M_F - K''_F}^{*F} \Phi_{\text{vesn}}^{(F, -K''_F)} \right\rangle \\ &= \left\langle D_{M_F K'_F}^{*F} \Phi_{\text{vesn}}^{(F, K'_F)} \middle| H \middle| D_{M_F K''_F}^{*F} \Phi_{\text{vesn}}^{(F, K''_F)} \right\rangle^*. \end{aligned} \quad (33.24)$$

The formula for matrix elements of optical transition operators can also be reanalyzed,

$$\begin{aligned} & \langle \psi^{F', M'_F + p} | T_p^{(L)}(\text{lab}) | \Phi^{F'', M''_F} \rangle \quad (33.25) \\ &= \left[\frac{(2F'' + 1)}{(2F' + 1)} \right]^{1/2} \langle F'' M''_F, L p | F' M'_F + p \rangle \\ & \times \frac{1}{2} \sum_{qK''} \langle F'' K''_F, L q | F' K'_F + q \rangle \\ & \times \left\{ \left\langle \psi_{\text{vesn}}^{(F', K''_F + q)} \middle| T_q^{(L)}(\text{body}) \middle| \Phi_{\text{vesn}}^{(F'', K''_F)} \right\rangle \right. \\ & \left. + (-1)^{F' + L - F''} \right. \\ & \left. \times \left\langle \psi_{\text{vesn}}^{(F', -K''_F - q)} \middle| T_{-q}^{(L)}(\text{body}) \middle| \Phi_{\text{vesn}}^{(F'', -K''_F)} \right\rangle \right\}, \end{aligned}$$

to establish that all contributions are purely real or purely imaginary [33.27]. Since such transition matrix elements will be used as absolute squares, they can be treated as if they were purely real.

Parity classification of molecular states according to inversion through the center of mass is important for establishing which transitions are electric-dipole allowed and which states can perturb each other. As discussed by Larsson [33.4], such classification is not without subtlety and opportunity for confusion. Inversion of the laboratory spatial coordinates (i_{sp} , also called E^* [33.2]) is equivalent to a reflection σ of the molecule-fixed electronic and nuclear coordinates in an arbitrary plane followed by rotation of the molecular frame by 180° about an axis through the origin and perpendicular to the reflection plane (if F is half-integral special care must be taken about the sense of rotation). It follows that

$$\begin{aligned} i_{\text{sp}} \Phi_{\text{exact}}^{F, M_F}(\text{lab}) &= E^* \Phi_{\text{exact}}^{F, M_F}(\text{lab}) \\ &= \eta (-1)^{F-\gamma} \Phi_{\text{exact}}^{F, M_F}(\text{lab}) \\ &= \left[\frac{(2F+1)}{8\pi^2} \right]^{1/2} \\ &\quad \times \sum_{K_F} (-1)^{F-K_F} D_{M_F-K_F}^{*F} \sigma_{xz} \Phi_{\text{vesn}}^{(F, K_F)} \end{aligned} \quad (33.26)$$

and

$$\sigma_{xz} \Phi_{\text{vesn}}^{(F, K_F)} = \eta (-1)^{K_F-\gamma} \Phi_{\text{vesn}}^{(F, -K_F)}, \quad (33.27)$$

where $\gamma = 0$ or $1/2$ for integral or half-integral F , respectively, and η is the parity label for the state, having values of ± 1 . In linear molecules, levels with $\eta = +1$ are called e -levels while those with $\eta = -1$ are called f -levels [33.28, 29].

Inversion symmetry can be combined with time reversal to establish that all matrix elements of the Hamiltonian can be taken to be real [33.27]. The wave function can also be expressed in the form of the Wang transformation [33.19], uniting the $\pm K_F$ components,

$$\begin{aligned} \Phi_{\text{exact}}^{F, M_F}(\text{lab}) &= \left(\frac{(2F+1)}{8\pi^2} \right)^{1/2} \sum_{K_F \geq 0} \left[D_{M_F K_F}^{*F} \Phi_{\text{vesn}}^{(F, K_F)} \right. \\ &\quad \left. + \eta (-1)^{-K_F+\gamma} D_{M_F - K_F}^{*F} \sigma_{xz} \Phi_{\text{vesn}}^{(F, K_F)} \right] \\ &\quad \times [2(1 + \delta_{K_F 0})]^{-1/2}. \end{aligned} \quad (33.28)$$

If the molecule is rigid and has a plane of symmetry, or is nonrigid with accessible vibrational or tunneling modes that correspond to plane reflections, in-

version symmetry divides the states of the molecule into two classes, according to the sign of η . Perturbations can occur only for $\Delta F = 0$ and $\eta' \eta'' = +1$. For optical transitions, the change in parity of the states must match the parity of the operator. Odd operators (e.g., electric-dipole) require $\eta' \eta'' (-1)^{\Delta F} = -1$. Even operators (e.g., magnetic-dipole and electric-quadrupole) require $\eta' \eta'' (-1)^{\Delta F} = +1$.

33.4.3 Nuclear Spin, Spatial Symmetry, and Statistics

For most molecules, the coupling of nuclear spin with the electron-spin, electron-orbital, and frame-rotational angular momenta is sufficiently weak that treatment of the energetics of hyperfine interactions can be postponed. The first-order effect of nuclear spin is that rovibronic wave functions for molecules containing identical nuclei must be combined with appropriate nuclear spin wave functions in order to obtain the necessary Fermi–Dirac or Bose–Einstein nuclear permutation symmetry. For many molecules, there exist combinations of nuclear permutations that correspond to combinations of frame rotations, laboratory inversions, and feasible vibrational motions (the rotational wave function makes a contribution because renumbering the nuclei requires a reanalysis of the Euler angles). For rigid molecules, these permutations (possibly including inversion) can be used to generate the point symmetry group of the molecule. For fluxional molecules, with multiple energetically equivalent nuclear configurations, a rather large “molecular symmetry group” can result, one that may not correspond to any ordinary point group [33.1, 2].

In the discussion immediately following, consider the case of N occurrences of one kind of nucleus, the others being unique (e.g., PD_3). The treatment can easily be extended to the case of multiple kinds of identical nuclei (e.g., C_2H_6). The exact wave function can be rearranged into a sum over products of the form

$$\Phi_{\text{exact}} = \sum_{a,b} \Phi_{\text{rves}}^{(a)} \Phi_{\text{nspin}}^{(b)}, \quad (33.29)$$

where $\Phi_{\text{rves}}^{(a)}$ is a rovibronic wave function belonging to the $\Gamma(a)$ representation of the symmetric group S_N of permutations over N objects, and $\Phi_{\text{nspin}}^{(b)}$ is a nuclear spin wave function, belonging to the $\Gamma(b)$ representation of S_N . In order to obtain the correct permutation symmetries for the overall wave function, the only terms that can appear in this sum are those for which the direct product $\Gamma(a) \otimes \Gamma(b)$ contains the symmetric or antisymmetric representation, for bosons or fermions, respectively.

Assumption of negligible hyperfine interactions allows evaluation of matrix elements of the form

$$\begin{aligned} & \langle \Phi_{\text{rves}}^{(c)} \Phi_{\text{nspin}}^{(d)} | H | \Phi_{\text{rves}}^{(a)} \Phi_{\text{nspin}}^{(b)} \rangle \\ &= \langle \Phi_{\text{rves}}^{(c)} | H | \Phi_{\text{rves}}^{(a)} \rangle \langle \Phi_{\text{nspin}}^{(d)} | \Phi_{\text{nspin}}^{(b)} \rangle, \end{aligned} \quad (33.30)$$

which vanishes unless $\Gamma(a) = \Gamma(c)$ and $\Gamma(b) = \Gamma(d)$. Thus the nearly-exact wave function can be written as a sum over products where the rovibronic and nuclear-spin factors correspond to basis functions from single known representations:

$$\Phi_{\text{exact}} \approx \sum_{a,b} \Phi_{\text{rves}}^{(a)} \Phi_{\text{nspin}}^{(b)}, \quad (33.31)$$

with $\Gamma(a) = \Gamma_{\text{rves}}$ and $\Gamma(b) = \Gamma_{\text{nspin}}$. This divides the states of the molecule into a number of noninteracting symmetry classes, labeled by the representations of the symmetric group. In the absence of hyperfine interactions, optical transitions are possible only within a certain symmetry class.

Thus the existence of spatial or dynamical symmetry implies that each rovibronic wave function transforms according to a particular representation of a subgroup of the permutation-inversion group (called CNPI by *Bunker* [33.2]). Each representation includes only specific values of nuclear spin, corresponding to the permutational properties of the nuclear spin wave functions. The most important effect of this analysis is to assign statistical weights or relative intensities to the different symmetry types. For example, the symmetry group for NH_3 is D_{3h} (including umbrella inversion), with representations A_1' , A_2' , A_1'' , A_2'' , E' , and E'' . The A_1' and A_1'' representations must be combined with the (nonexistent) antisymmetric spin function, yielding a statistical weight of 0. Similarly, A_2' and A_2'' combine with the symmetric $I = 3/2$ spin function, with a statistical weight of 4 (i.e., $2I + 1$). E' and E'' combine with the nonsymmetric $I = 1/2$ spin functions, with a statistical weight of 2. This material is discussed from various viewpoints in numerous articles and text books, of which only a few can be cited here [33.1, 2, 8, 18, 21, 30–36]. See Chapt. 32 for additional details and examples.

Although this analysis appears rather complicated, the selection rules that result are actually the same, at least in simple cases, as the ones that are derivable from simpler ideas. For example, for a ${}^1\Sigma_g^+$ lower state, even J levels are permutation symmetric and have parity $+1$, while odd J levels are permutation antisymmetric and have parity -1 . For a ${}^1\Sigma_u^+$ upper state, even J levels are permutation antisymmetric and

have parity $+1$, while odd J levels are permutation symmetric and have parity -1 . Both the parity selection rule and permutation-symmetry selection rule independently require that $\Delta J = \pm 1$ for electric-dipole transitions. Similarly, that the permanent dipole moment of a symmetric-top molecule must lie along the body-fixed axis replicates the $\Delta K = 0$ selection rule for pure-rotation transitions provided by permutational symmetry arguments. This means that when simulating absorption and emission spectra, the nuclear-spin wave function can usually be ignored. The intensity alternation imposed by spin-statistics can be represented by multiplying each wave function by the appropriate factor, for example, 0 or $[(2I + 1)/(2i + 1)]^{1/2}$, where I is the total nuclear spin, and i is the spin of one of the N equivalent nuclei.

Group theory remains vital for understanding the relative strengths of vibrational transitions in polyatomics (see *Cotton* [33.37], for example, and Sect. 33.6.2) and becomes very interesting as interaction between vibration and rotation increases. For the purposes of this discussion, the most important issue is identification of which transition-moment matrix elements $\mu_{K'K''}$ vanish and which are related by symmetry.

33.4.4 Electron Orbital and Spin Angular Momenta

For all molecules, the strongest transitions tend to be those that conserve electron spin. The zero-order transition-moment matrix is diagonal both in total spin and in spin-projection onto the body-frame axis. In the $|\Lambda\Sigma\rangle$ basis set for linear molecules this is expressed by

$$\mu_{\Lambda'\Sigma'\Lambda''\Sigma''} = \mu_{\Lambda'\Lambda''} \delta_{\Sigma'\Sigma''}. \quad (33.32)$$

The transition-moment tensor operator $T_q^{(L)}$ (body) can connect basis functions that differ in Λ by at most L . Allowed electric-dipole transitions thus satisfy

$$\mu_{\Lambda'\Lambda''} = 0, \quad \text{for } |\Lambda' - \Lambda''| > 1. \quad (33.33)$$

In the usual case that the upper and lower states each consist of only a single value of $|\Lambda|$, there is only one independent, nonzero, matrix element $\mu_{|\Lambda'|,|\Lambda''|}$ with

$$\mu_{-|\Lambda'|,-|\Lambda''|} = \eta(-1)^{|\Lambda'|+|\Lambda''|} \mu_{|\Lambda'|,|\Lambda''|}. \quad (33.34)$$

See Sect. 33.8 for a discussion of spin-forbidden and orbitally-forbidden transitions. Similar arguments and phase relationships can be developed for polyatomic molecules with nonzero electron spin or degenerate vibrational or electronic states.

33.5 Absorption Cross Sections and Radiative Lifetimes

33.5.1 Radiation Relations

Among the most important radiation relations is the connection between the absorption cross section and the rate of spontaneous emission. *Einstein* [33.38] introduced his A and B coefficients to describe the rates of absorption and emission of radiation of a collection of two-level atoms or molecules in equilibrium with a radiation field at the same temperature. The discussion here follows that of *Condon and Shortley* [33.39], *Penner* [33.40], *Thorne* [33.41], and *Steinfeld* [33.42] (with corrections). Also see Chaps. 10, 17, and 68 of this Handbook. The number of absorption events per unit volume per unit time is written as

$$N_l B_{lu} \rho(\nu) . \quad (33.35)$$

While the rate of emission is

$$N_u B_{ul} \rho(\nu) + N_u A_{ul} . \quad (33.36)$$

In thermal equilibrium, the radiative energy density is given by the Planck blackbody law

$$\rho(\nu) = \left(\frac{8\pi h \nu^3}{c^3} \right) (e^{h\nu/kT} - 1)^{-1} , \quad (33.37)$$

and the ground and excited state densities satisfy a Boltzmann relationship,

$$\frac{N_u}{N_l} = \left(\frac{g_u}{g_l} \right) e^{-h\nu/kT} , \quad (33.38)$$

where g_u and g_l are the degeneracies of the upper and lower states. The requirement that the rates of absorption and emission must be equal leads to the relations

$$A_{ul} = \left(\frac{8\pi h \nu^3}{c^3} \right) B_{ul} = \left(\frac{8\pi h \nu^3}{c^3} \right) \left(\frac{g_l}{g_u} \right) B_{lu} . \quad (33.39)$$

Numerical values of the B coefficients can be derived from the optical absorption cross section, and thus

$$\begin{aligned} A_{ul} &= \left(\frac{8\pi \nu^2}{c^2} \right) \left(\frac{g_l}{g_u} \right) \int \sigma_{\text{abs}}(\nu) \, d\nu \\ &= \left(\frac{8\pi \nu^2}{c^2} \right) \int \sigma_{\text{se}}(\nu) \, d\nu . \end{aligned} \quad (33.40)$$

Finally, the expression for the absorption oscillator strength is

$$\begin{aligned} f_{\text{abs}} &= (4\pi\epsilon_0) \left(\frac{mc^3}{8\pi^2 \nu^2 e^2} \right) \left(\frac{g_l}{g_u} \right) A_{ul} \\ &= (4\pi\epsilon_0) \left(\frac{mc}{\pi e^2} \right) \int \sigma_{\text{abs}}(\nu) \, d\nu . \end{aligned} \quad (33.41)$$

The emission oscillator strength is simply related to that for absorption: $f_{\text{em}} = -(g_l/g_u) f_{\text{abs}}$. The oscillator strength offers considerable advantages as a means of reporting and comparing the strengths of radiative transitions. It is dimensionless, obeys the simple sum rule (for electric-dipole transitions)

$$\sum_u f_{ul} = \text{number of electrons} , \quad (33.42)$$

and is directly derivable from an experimental absorption cross section even before the assignment of the upper level has been determined (i. e., before its degeneracy is known).

33.5.2 Transition Moments

In many cases, the intention is to construct model quantum mechanical wave functions for the two states involved in the transition under study. In addition, ab initio electronic wave functions and matrix elements may be available (see Chapt. 31). Quantum mechanics suggests the following expression for the Einstein A coefficient (see Sect. 11.5.1):

$$\begin{aligned} A_{ul} &= \left(\frac{64\pi^4 \nu^3}{3hc^3} \right) \left(\frac{1}{4\pi\epsilon_0} \right) \left(\frac{1}{g_u} \right) \\ &\times \sum_{u', l'', p} | \langle \psi'_{u'} | e r_p | \psi''_{l''} \rangle |^2 . \end{aligned} \quad (33.43)$$

The summation is over all three optical polarization directions p (i. e., r_p runs over x , y , and z in the lab frame), all degenerate components l'' of the lower state (i. e., g_l of them), and all degenerate components u' of the upper state (i. e., g_u of them). This triple sum is also called the *line strength* S_{ul} . Division by the upper-level degeneracy corrects for the fact that the transitions should be averaged rather than summed over the initial levels.

In practice, choosing the appropriate degeneracy to divide by is a question of some ambiguity. For atoms, it is sufficient to understand how the individual matrix elements and the line strength were calculated. For example, *Bethe and Salpeter* [33.43] use a degeneracy of $(2L + 1)$ for Schrödinger wave functions for the hydrogen atom, and $(2J + 1)$ for Dirac wave functions.

For molecules with internal angular momentum, i. e., everything other than $^1\Sigma$ states of linear molecules, the situation is much more complicated. For electric-dipole allowed transitions in light molecules, ab initio transition moments are calculated in a body-fixed coordinate system, ignoring spin, and not summed over anything.

For diatomic molecules, following the work of *Whiting* et al. [33.44, 45], the transition probability from a single upper-state component ($J'c'$) to a single lower-state component ($J''c''$) is written as

$$A_{J'c'J''c''} = \left(\frac{64\pi^4\nu^3}{3hc^3} \right) \left(\frac{1}{4\pi\epsilon_0} \right) \times \left(\frac{1}{2J'+1} \right) q_{v'v''} |R_e|^2 S_{J'J''}^{c'c''}. \quad (33.44)$$

In this formula $q_{v'v''}|R_e|^2$ represents the rotationless contribution to the transition moment, symbolically represented as a product of a vibrational overlap ($q_{v'v''}$, i. e., a Franck–Condon factor) and an electronic-only component $|R_e|^2$ (Sect. 33.6.1). All of the rotational complexity is absorbed into the rotational-branch strength factor $S_{J'J''}^{c'c''}$ (Sects. 33.7.2 and 33.7.3). The issue to be addressed here is how to divide numerical factors between $|R_e|^2$ and $S_{J'J''}^{c'c''}$. One approach is to construct an estimate for the rotationless transition probability

$$A_{v'v''} = \left(\frac{1}{N'_c} \right) \sum_{c'J'c''} A_{J'c'J''c''}, \quad (33.45)$$

where N'_c is the number of internal spin-orbit components of the upper state. *Whiting* et al. suggest that $S_{J'J''}^{c'c''}$

be normalized such that for spin-allowed transitions

$$\sum_{c'J'c''} S_{J'J''}^{c'c''} = (2 - \delta_{0,\Lambda'}\delta_{0,\Lambda''})(2S+1)(2J'+1). \quad (33.46)$$

The first factor is 1 for Σ – Σ transitions, and 2 for all others. The final factor is replaced by $(2J''+1)$ if the sum is over J' instead of J'' . For spin-forbidden transitions the following is a plausible extension of this sum rule,

$$\sum_{c'J'c''} S_{J'J''}^{c'c''} = \max(N'_c, N''_c)(2J'+1). \quad (33.47)$$

Section 33.7.3 provides a corresponding sum rule for polyatomic molecules. This normalization yields

$$A_{v'v''} = \left(\frac{64\pi^4\nu^3}{3hc^3} \right) \left(\frac{1}{4\pi\epsilon_0} \right) \times \left(\frac{\max(N'_c, N''_c)}{N'_c} \right) q_{v'v''} |R_e|^2 \quad (33.48)$$

and for spin-allowed transitions, the simple spin-free expressions for the electronic transition moments:

$$|R_e|^2 = |\langle \Lambda | e z | \Lambda \rangle|^2 \quad (33.49)$$

for parallel transitions and

$$|R_e|^2 = \left| \langle \Lambda + 1 | e \frac{1}{\sqrt{2}}(x + iy) | \Lambda \rangle \right|^2 \quad (33.50)$$

for perpendicular transitions.

33.6 Vibrational Band Strengths

33.6.1 Franck–Condon Factors

The Born–Oppenheimer separation of electron and nuclear motion suggests that during an optical transition between different electronic states the nuclei should change neither their position nor momentum. This concept was developed from semiclassical arguments by *Franck* [33.46] and justified quantum mechanically by *Condon* [33.47]. Following *Herzberg* [33.48] and *Steinfeld* [33.42] the vibronic transition moment can be written as

$$\begin{aligned} \mu_{v'v''} &= \langle \psi'_e \psi'_{v'} | \mu | \psi''_e \psi''_{v''} \rangle, \\ &= \int dR \psi_{v'}^{*'}(R) \psi''_{v''}(R) \\ &\quad \times \int dr \psi_e^{*'}(r, R) \psi_e''(r, R) \mu(r, R), \\ &= \int dR \psi_{v'}^{*'}(R) \psi''_{v''}(R) \mu(R). \end{aligned} \quad (33.51)$$

If the R -dependence of $\mu(R)$ is sufficiently weak, it can be factored out to obtain

$$\mu_{v'v''} = R_e \int dR \psi_{v'}^{*'}(R) \psi''_{v''}(R), \quad (33.52)$$

where R_e is called the electronic transition moment. The transition probability is proportional to the square of the above, which is usually written as

$$I \approx q_{v'v''} R_e^2, \quad (33.53)$$

where

$$q_{v'v''} = \left| \int dR \psi_{v'}^{*'}(R) \psi''_{v''}(R) \right|^2, \quad (33.54)$$

the square of the overlap between initial and final vibrational wave functions, is called the Franck–Condon factor.

The Franck–Condon factors satisfy the sum rule

$$\sum_{v'} q_{v'v''} = \sum_{v''} q_{v'v''} = 1 \quad (33.55)$$

provided the summations include the continuum vibrational wave functions above the dissociation limits. The Franck–Condon approach also can be used to calculate intensities and cross sections for bound–free [33.49] and free–free [33.50] emission and absorption.

In some cases the variation of $\mu(R)$ is significant. Calculation of the effect on the intensities can usually be handled by the *r*-centroid method in which the expression

$$\bar{r}_{v'v''} = \frac{\langle \psi_{v'}' | R | \psi_{v''}'' \rangle}{\langle \psi_{v'}' | \psi_{v''}'' \rangle} \quad (33.56)$$

is used to calculate an effective internuclear distance for the transition. The transition strength is then proportional to $q_{v'v''} |\mu(\bar{r}_{v'v''})|^2$. An advantage of this formulation is that the vibrational overlaps can be calculated from energy information only, before the transition moment function is known and before the transition strengths are investigated experimentally. The quantitative accuracy of the *r*-centroid method for transition moments that are not linear in the internuclear distance, has been addressed by a considerable literature, which has been summarized by *McCallum* [33.51].

A second complication arises from the fact that the vibrational wave functions themselves depend parametrically on the rotational angular momentum. Calculation of rotationally-dependent Franck–Condon factors is described by *Dwivedi* et al. [33.52] who also discuss the *r*-centroid method.

33.6.2 Vibrational Transitions

Vibrational transitions derive their strength from the variation of the “permanent” dipole moment of the

33.7 Rotational Branch Strengths

33.7.1 Branch Structure and Transition Type

The overall rotational structure of a molecular transition is determined by the relative values and phases of the body–frame transition-moment matrix elements, the relative values and phases of coefficients in the expansion of the upper-state and lower-state component wave functions over the angular-momentum-projection basis functions, the energy separations between the components, and the relative values and phases of the vector-coupling coefficients. In simple cases, each lower component might be connected to only a single upper component [Hund’s case (b) or symmetric tops],

molecule as a function of geometry or internuclear coordinates. As described by several authors [33.31, 32, 34, 53] one can expand the dipole moment as a power series in the internal-Cartesian or normal-mode coordinates

$$M_{xyz}(Q) = M_{xyz}^0 + \sum_i \left(\frac{\partial M_{xyz}}{\partial Q_i} \right) Q_i + \dots \quad (33.57)$$

and calculate intensities from a formula like

$$I \approx |\langle \psi_{v_1}' \psi_{v_2}'' \dots | M(Q) | \psi_{v_1}' \psi_{v_2}'' \dots \rangle|^2. \quad (33.58)$$

For homonuclear diatomic molecules, the dipole moment vanishes identically, so there is no vibrational spectrum. The dipole moment for heteronuclear diatomics is often close to linear in the internuclear distance. The harmonic oscillator model suggests that transitions with $\Delta v = \pm 1$ are the strongest, with intensities approximated by

$$I_{v+1,v} \approx \left| \frac{dM}{dR} \right|^2 (v+1). \quad (33.59)$$

Overtone bands, i.e., with $|\Delta v| > 1$, are observed, as dramatically illustrated by the $\Delta v = 4, 5$ emissions from the OH radical observed from the Earth’s night sky [33.54].

For polyatomic molecules, overtone and combination bands are often quite strong. The presence or absence of which is used to establish the symmetries of the vibrational modes. In general, it is difficult to construct quantitative vibrational intensity formulas with only a few parameters that can be inferred experimentally.

or $\Delta J = \pm 1$ (*P*- and *R*-branches) may dominate over $\Delta J = 0$ (*Q*-branches).

For diatomic molecules, symmetry arguments are used to divide the components into the two parity classes *e* and *f*. For electric dipole transitions, the selection rules from Sect. 33.4.2 imply that

$$\begin{array}{ll} (N_e' N_e'' + N_f' N_f'') & P\text{- and } R\text{-branches} \\ (N_e' N_f'' + N_f' N_e'') & Q\text{-branches} \end{array} \quad (33.60)$$

are expected, where N_e and N_f indicate the number of components of each parity class (N_e and N_f differ by no more than one). Rotational branches are labeled with

the notation ${}^{\Delta R}\Delta J_{c'c''}$, using symbols P for -1 , Q for 0 , and R for $+1$. ΔR indicates the “apparent” change in mechanical rotational angular momentum (i. e., energy) [see Hund’s case (b) in Sect. 33.7.4] and ΔJ indicates the “actual” change (i. e., quantum mechanical). The labels $c'c''$ indicate the components involved. Thus a ${}^P Q_{21}$ branch is expected to be “red shaded” ($\Delta R = -1$) with $\Delta J = 0$ involving the second component of the upper state and the first (lowest) component of the lower state. The notation ${}^P Q_{21}(J)$ [or sometimes ${}^P Q_{21}(R = N)$ for Σ lower states] identifies an individual rotational line and specifies the rotational quantum number of the lower state involved in the transition. If the upper- and lower-state component numbers are the same, one of them may be dropped. Thus P_{22} is sometimes written as P_2 .

For symmetric top molecules, the rotational branches are labeled ΔJ_K (e.g., P_1). For asymmetric tops, the branches are labeled by $\Delta J_{\Delta K_{-1}, \Delta K_1}$, where K_{-1} and K_1 are the prolate- and oblate-limit angular momenta projections (described in Sect. 33.3.2).

The transition dipole moment commonly lies parallel or perpendicular to the body-frame axis. In the former case, $\mu_{K'K''}$ vanishes for $K' \neq K''$, and in the latter for $K' = K''$. Thus parallel bands correspond to $\Delta K = 0$ transitions, while perpendicular bands have $\Delta K = \pm 1$. As enforced by the vector-coupling coefficients or Hönl–London factors described below, for low values of K (e.g., diatomics), $\Delta K = 0$ implies strong $\Delta J = \pm 1$ (P and R) branches and weak $\Delta J = 0$ (Q) branches. On the other hand, $\Delta K = \pm 1$ leads to Q -branches that are approximately twice as strong as either the P - or R -branches.

33.7.2 Hönl–London Factors

The matrix model Hamiltonians for the upper and lower states have been diagonalized, yielding the wave functions

$$\begin{aligned} \psi_{c'}^{J'M'} &= \sum_{K'} b_{J'c'}^{K'} \left(\frac{(2J'+1)}{8\pi^2} \right)^{1/2} \\ &\times D_{M'K'}^{*J'}(\text{lab}) \chi_{K'}(\text{body}) \end{aligned} \quad (33.61)$$

and

$$\begin{aligned} \Phi_{c''}^{J''M''} &= \sum_{K''} a_{J''c''}^{K''} \left(\frac{(2J''+1)}{8\pi^2} \right)^{1/2} \\ &\times D_{M''K''}^{*J''}(\text{lab}) \xi_{K''}(\text{body}). \end{aligned} \quad (33.62)$$

In these expressions, the designations K' and K'' are slightly symbolic. They represent the body-frame projection of the total angular momentum and also a running index over basis functions. For complicated cases, more than one basis function can have a given value of K .

Following Sect. 33.2.3, the rotational branch strength is then written as

$$\begin{aligned} S_{J'J''}^{c'c''} &= \sum_{pM'M''} |\langle \psi_{c'}^{J'M'} | T_p^{(L)}(\text{lab}) | \Phi_{c''}^{J''M''} \rangle|^2 \\ &= (2J''+1) \left| \sum_{q'K'K''} b_{J'c'}^{*K'} a_{J''c''}^{K''} \langle \chi_{K'} | T_q^{(L)}(\text{body}) | \xi_{K''} \rangle \right. \\ &\quad \left. \times \langle J''K'', Lq | J'K' \rangle \right|^2 \end{aligned} \quad (33.63)$$

or

$$S_{J'J''}^{c'c''} = \left| \sum_{K'K''} b_{J'c'}^{*K'} a_{J''c''}^{K''} \mu_{K'K''} \zeta(J', K', J'', K'') \right|^2, \quad (33.64)$$

where

$$\mu_{K'K''} = \langle \chi_{K'} | T_q^{(L)}(\text{body}) | \xi_{K''} \rangle \theta(K'' - K') \quad (33.65)$$

is the body-frame transition-moment matrix introduced in Sect. 33.3.4, with relative values that are hypothesized based on interpretation of the nature of the transition, calculated from ab initio wave functions, or inferred by fitting the observed rotational branch strengths. The Clebsch–Gordan expression

$$\begin{aligned} \zeta(J', K', J'', K'') &= (2J''+1)^{1/2} \langle J''K'', LK' - K'' | J'K' \rangle \\ &\times \theta(K'' - K') \theta(J' - J'') \end{aligned} \quad (33.66)$$

represents the transformation of the radiation field from the laboratory-frame to the body-frame, also related to the “direction cosines” used by many authors. The additional phase factors

$$\theta(k) = \text{sgn}(k) = \begin{cases} +1 & k \geq 0 \\ -1 & k < 0 \end{cases} \quad (33.67)$$

have been included here to make the signs and symmetry relations of $\mu_{K'K''}$ and $\zeta(J', K', J'', K'')$ agree with those already in use [33.9, 44, 55, 56]. They are related to the choice of the leading signs when T_+ and T_- are expressed as $\pm(T_x + iT_y)$ and $\pm(T_x - iT_y)$. Their inclusion has no effect for spin-allowed transitions with only

one source of transition probability, e.g., purely parallel or perpendicular.

In the usual case of electric-dipole (or magnetic-dipole) radiation (i.e., $L = 1$), ζ^2 is the well-known Hönl–London factor [33.57]. $\zeta(J', K', J'', K'')$ is a real, signed quantity: negative for $\Delta J \Delta K > 0$; or $\Delta J = \Delta K = 0$ and $K < 0$; otherwise positive [33.9].

Setting $L = 2$ provides intensity formulas for electric-quadrupole [33.58], Raman [33.59], and two-photon [33.60, 61] transitions. Additional Rayleigh-like terms can appear for $K' = K'' \neq 0$. Halpern et al. [33.61] also give formulas for three-photon transitions in diatomics, expressed in terms of Clebsch–Gordan coefficients with $L = 3$ and $L = 1$ (for $|\Delta\Omega| \leq 1$).

33.7.3 Sum Rules

The orthonormality relations for component eigenvectors

$$\sum_{c'} b_{J'c'}^{*K'} b_{J'c'}^K = \delta_{K',K}, \quad (33.68)$$

$$\sum_{c''} a_{J''c''}^{*K''} a_{J''c''}^K = \delta_{K'',K} \quad (33.69)$$

can be used to construct the sum rule

$$\sum_{c'c''} S_{J'J''}^{c'c''} = \sum_{K'K''} |\mu_{K'K''} \zeta(J', K', J'', K'')|^2. \quad (33.70)$$

Finally, the orthonormality relations of the Clebsch–Gordan coefficients result in

$$\sum_{J'c'c''} S_{J'J''}^{c'c''} = (2J'' + 1) \sum_{K'K''} |\mu_{K'K''}|^2, \quad (33.71)$$

$$\sum_{J''c'c''} S_{J'J''}^{c'c''} = (2J' + 1) \sum_{K'K''} |\mu_{K'K''}|^2. \quad (33.72)$$

As discussed in Sect. 33.5.2, it is convenient to have the $\mu_{K'K''}$ matrix elements consist of numbers that represent the nature of the transition but not its strength, the latter being expressed by the “vibrational” ($q_{v'v''}$) and “electronic” (R_e) contributions. Following Sect. 33.5.2, for diatomic molecules, the “orientational” part $\mu_{K'K''}$ is taken to have a fixed sum rule

$$\sum_{K'K''} |\mu_{K'K''}|^2 = \max(N'_c, N''_c), \quad (33.73)$$

where N'_c is the number of components (K' values, or basis functions) for the upper state, and N''_c is the number of components in the lower state. For polyatomic molecules, the sum rule can be written as

$$(2J + 1)^2 (\mu_a^2 + \mu_b^2 + \mu_c^2) \max(N'_c, N''_c), \quad (33.74)$$

where

$$\mu_a^2 + \mu_b^2 + \mu_c^2 = |\mu_+|^2 + |\mu_-|^2 + |\mu_0|^2 = 1 \quad (33.75)$$

and N'_c and N''_c are the numbers of spin-electronic-vibrational components in the upper and lower states, respectively. Also see Whiting et al. [33.44, 45] and Brown et al. [33.7].

33.7.4 Hund's Cases

In diatomic molecules, several limiting cases are useful as short-hand or first-approximation concepts for classification of energy levels and rotational branch strengths. These are called the Hund's cases [33.62–64]. They are distinguished by the extent to which the electron orbital and spin angular momenta are rigidly attached to the tumbling molecular frame, i.e., whether Λ , Σ , and S are good quantum numbers. Hund's cases are discussed in many journal articles and in every textbook dealing with the rotational structure of diatomic spectra. An appealing recent description is provided by Nikitin and Zare [33.65].

In most works, the emphasis has been on finding a favorable zero-order approximation for perturbation expansion of energy levels. The advance of precision measurement of transition energies and the availability of sophisticated parametrical matrix models and fast computers on which to realize them, has reduced the importance of Hund's cases for actual computations. In particular, the need to derive and implement numerous explicit energy and intensity formulas leads to unfortunate transcription errors. Nevertheless, they remain of value for qualitative and pedagogical understanding, especially for estimates of the relative intensities of rotational branches.

Hund's case (a) describes the situation in which Λ and Σ are separately well-defined. This is a common case in which the separation between electronic states, i.e., different values of $|\Lambda|$, is larger than the spin-orbit interaction, which in turn, is larger than the separation between rotational levels. At low J , there are $(2S + 1)$ pairs of nearly-degenerate energy levels separated from each other by the spin orbit constant: $E \approx A\Lambda\Sigma +$

$BJ(J+1)$. The wave functions are of the form

$$\begin{aligned} \psi_{\Omega\pm}^{JM} &= \frac{1}{\sqrt{2}} \left(\frac{(2J+1)}{8\pi^2} \right)^{1/2} \\ &\times \left[D_{M\Lambda+\Sigma}^{*J} |\Lambda, \Sigma\rangle \pm D_{M-\Lambda-\Sigma}^{*J} |-\Lambda, -\Sigma\rangle \right] \\ &= \frac{1}{\sqrt{2}} [|\Lambda, \Sigma; J, M, \Omega\rangle \\ &\quad \pm |-\Lambda, -\Sigma; J, M, -\Omega\rangle], \end{aligned} \quad (33.76)$$

with only two nonzero expansion coefficients a_{Jc}^K . If both the upper and lower states are well described by Hund's case (a), then each lower component is optically connected only to the upper components with the same value of $|\Sigma|$. Then

$$S_{J'J''}^{\Omega'\Omega''} = (2J''+1) |\langle J''\Omega'', 1\Omega' - \Omega | J'\Omega'\rangle|^2, \quad (33.77)$$

with $\Omega'' = \Lambda' + \Sigma$ and $\Omega' = \Lambda' + \Sigma$.

Hund's case (b) indicates that Λ is well-defined, but spin-orbit coupling is weak. The components correspond to well-defined values of $N = J - S$, ranging from $|J - S|$ to $(J + S)$, with energies approximated by $E \approx BN(N+1)$, and wave functions of the form

$$\begin{aligned} \psi_{N\pm}^{JM} &= \sum_{\Sigma} (-1)^{S+\Sigma} \langle J - \Omega, S\Sigma | N - \Lambda \rangle \\ &\times \frac{1}{\sqrt{2}} [|\Lambda, \Sigma; J, M, \Omega\rangle \\ &\quad \pm |-\Lambda, -\Sigma; J, M, -\Omega\rangle]. \end{aligned} \quad (33.78)$$

This equation is derivable from Mizushima's equation (2-3-26) [33.14] and Zare's equations (2.8), (2.26), and (3.105) [33.5], using the lab-to-body transformation

$$|SM_S\rangle(\text{lab}) = \sum_{\Sigma} D_{M_S\Sigma}^{*S}(\phi\theta\chi) |S\Sigma\rangle(\text{body}). \quad (33.79)$$

It disagrees with Judd's problem 9.1 [33.66] by a phase factor $(-1)^{J+2S+\Sigma-N}$ but agrees with Mizushima's expansion of a $^3\Pi$ state [33.14, p. 287] if the Clebsch-Gordan coefficients are taken from *Condon and Shortley* [33.39, p. 76].

If both the upper and lower states are well described by Hund's case (b), these wave functions can be substituted into the general rotational-branch strength equations above. Following *Edmonds* [33.67, (6.2.8) and (6.2.13), and Table 5] yields the square of a product of Clebsch-Gordan and Racah coefficients

$$\begin{aligned} S_{J'J''}^{N'N''} &= (2J''+1)(2J'+1)(2N''+1) \\ &\times |\langle N''\Lambda'', 1\Lambda' - \Lambda'' | N'\Lambda' \rangle \\ &\times W(N', J'', N'', J'; S, 1)|^2. \end{aligned} \quad (33.80)$$

The Clebsch-Gordan coefficient enforces the case (b) selection rule $\Delta N = 0, \pm 1$, while the Racah coefficient provides the $\Delta J = \Delta N$ propensity rule, which becomes more precise as N increases. A similar propensity rule, $\Delta F = \Delta J$, is common for transitions between hyperfine components (see also *Ferminias* [33.68]).

Hund's case (c) corresponds to the situation in which spin-orbit coupling is so strong that each level described by the projection Ω actually consists of multiple values of $|\Lambda|$ (e.g., mixing of Σ and Π states) or multiple values of S (e.g., mixing of singlet and triplet spins). This limiting case is formally similar to Hund's case (a), but no assumptions can be made about the relative magnitudes of transition-moment matrix elements $\mu_{\Omega'\Omega''}$. Any of which can be nonzero for $|\Delta\Omega| \leq 1$, for example

$$\begin{aligned} S_{J'J''}^{\Omega'\Omega''} &= \frac{1}{4} |\mu_{\Omega'\Omega''} \zeta(J', \Omega', J'', \Omega'') \\ &\quad \pm \mu_{\Omega' - \Omega''} \zeta(J', \Omega', J'', -\Omega'') \\ &\quad + \mu_{-\Omega'\Omega''} \zeta(J', -\Omega', J'', \Omega'') \\ &\quad \pm \mu_{-\Omega' - \Omega''} \zeta(J', -\Omega', J'', -\Omega'')|^2. \end{aligned} \quad (33.81)$$

The symmetry (sign) relations between $\mu_{\Omega'\Omega''} \zeta(J', \Omega', J'', \Omega'')$ and $\mu_{-\Omega' - \Omega''} \zeta(J', -\Omega', J'', -\Omega'')$ determine whether this transition occurs only for $\Delta J = \pm 1$ (P - and R -branches) or only for $\Delta J = 0$ (Q -branches).

The interest and complexity of Hund's case (c) were exemplified by a seminal work by *Kopp and Hougen* [33.69], who considered $\Omega' = 1/2$, $\Omega'' = 1/2$ transitions, under the assumption that both states could consist of arbitrary mixtures of $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ character. Each of the six rotational branches shows constructive or destructive interference of parallel ($\Delta\Omega = 0$) and perpendicular ($\Delta\Omega = \pm 1$) contributions. Hund's case (c) also describes spin-orbit mixing collisions [33.70] or dissociation to specific spin-orbit limits [33.71–73].

Hund's case (d) arises in the investigation of Rydberg series [33.74], in which the separation between Σ and Π from the same orbital configuration approach each other as the principal quantum number (n) increases. Spin-orbit coupling between these projections also diminishes. The eigenfunction components correspond to well-defined values of $R = J - L$, ranging from $|J - L|$ to $(J + L)$, with energies approximated by $E \approx BR(R+1)$, and wave functions of the

form

$$\psi_{RL}^{JM} = \sum_{\Lambda} (-1)^{L+\Lambda} \langle J-\Lambda, L\Lambda | R0 \rangle | L\Lambda; JM \Lambda \rangle. \quad (33.82)$$

Carroll [33.74] used intensity formulas provided by Kovacs [33.58] to analyze, by spectral simulation, the 4p–15p ($^1\Sigma_u^+$ and $^1\Pi_u$) Rydberg states of N_2 excited from the ground $X^1\Sigma_g^+$. Three strong Q -form branches survive, corresponding to $R' = J''$, two arising from $\Pi \leftarrow \Sigma$ and one from $\Sigma \leftarrow \Sigma$ case (a) branches. The remaining O -form ($R' = J'' - 2$) and S -form ($R' = J'' + 2$) branches fade rapidly as n increases. With the phase conventions used here, this situation corresponds to body-frame transition matrix elements satisfying

$$\mu_{00} = \mu_{-10} = -\mu_{10}. \quad (33.83)$$

In the opposite case, corresponding to a parity change of the parent-ion core [33.73], two of the Q -form branches are extinguished, while one Q -form, one O -form, and one S -form branch remain. The transition matrix elements would satisfy

$$\mu_{00} = 0, \quad \mu_{-10} = \mu_{10}. \quad (33.84)$$

Hund's case (d) polyatomics are also known [33.8].

Hund's case (e) would correspond to a situation in which L and S are strongly coupled to each other, but neither is strongly coupled to the internuclear axis. No examples are known for bound states of molecules.

33.7.5 Symmetric Tops

For transitions between nondegenerate vibronic states, the transition moment must lie along the principal top axis, leading to the selection rule $\Delta K = 0$. Otherwise, Hougen's convenient quantum number [33.33] $G = \Lambda + l - K$, provides the selection rule $\Delta G = 0, \pm n$ (for an

n -fold major symmetry axis) (Sects. Section 33.3.2, Section 33.4.3, and Chapt. 32). Transitions with $\Delta G = \pm n$ are much weaker than those with $\Delta G = 0$ and are not calculable from a simple formula. Branch intensities can be calculated with the Hönl–London formulas of Sect. 33.7.2.

33.7.6 Asymmetric Tops

In general, no assumptions can be made about the orientation of the transition moment. The vector representations (μ_x, μ_y, μ_z) , (μ_a, μ_b, μ_c) , and $(\mu_0, \mu_{+1}, \mu_{-1})$ can have any combination of independent nonzero values. It is common that one of the (μ_a, μ_b, μ_c) values is significantly larger than the others, especially for planar molecules with a two-fold symmetry axis. In this case one obtains a type A , B , or C band, if μ_a , μ_b , μ_c dominates, respectively [33.31, 75]. The tradition of analytic calculation of line strengths from explicit representations of wave functions and transition moments leads to formulas of considerable complexity, with somewhat restrictive assumptions [33.35, 36, 76]. In the more general notation of Sect. 33.7.2, the rotational line strength can be written as

$$S_{J'J''}^{\tau'\tau''} = \left| \sum_{K'K''} b_{J'\tau'}^{*K'} a_{J''\tau''}^{K''} (\mu_0 \delta_{K'K''} + \mu_+ \delta_{K'K''+1} + \mu_- \delta_{K'K''-1}) \zeta(J', K', J'', K'') \right|^2, \quad (33.85)$$

where

$$\begin{aligned} \mu_0 &= \mu_c, & |\mu_+| &= |\mu_-|, \\ |\mu_+|^2 + |\mu_-|^2 &= \mu_a^2 + \mu_b^2. \end{aligned} \quad (33.86)$$

Papoušek and Aliev [33.18] and Zare [33.5] follow the present formulation, but with somewhat less generality with respect to wave function expansion coefficients or transition moment components.

33.8 Forbidden Transitions

33.8.1 Spin-Changing Transitions

The formalism presented above permits simulation of any allowed transition or forbidden transitions mediated by spin-orbit or spin-spin perturbations, or any perturbation that is diagonal in Ω . For spin-allowed transitions, the transition moment matrix is taken to be

diagonal in and independent of the spin projection, so that

$$\mu_{\Lambda' \Sigma' \Lambda'' \Sigma''} = \mu_{\Lambda' \Lambda''} \delta_{\Sigma' \Sigma''}. \quad (33.87)$$

For forbidden transitions, or complicated Hund's case (c) mixings, the transition moment matrix elements can be considered as independent variable parameters,

limited only by the symmetry constraint

$$\mu_{-\Omega' - \Omega''} = \eta(-1)^{\Omega' - \Omega''} \mu_{\Omega' \Omega''}, \quad (33.88)$$

and the fact that terms with $|\Delta\Omega| > 1$ will be multiplied by zero. Alternatively, a specific set of candidate perturbers can be selected, and the Λ - and Σ -dependence of their contributions to the transition-moment matrix evaluated explicitly. For example, first-order spin-orbit mixing would lead to terms of the form

$$\begin{aligned} & \mu_{\Lambda' \Sigma' \Lambda'' \Sigma''}^{S' S''} \\ &= \sum_{\Lambda} \left[\mu_{\Lambda' \Sigma' \Lambda \Sigma'}^{S' S'} \frac{\langle S' \Lambda \Sigma' | H_{SO} | S'' \Lambda'' \Sigma'' \rangle}{\Delta E''} \right. \\ & \quad \left. + \left(\frac{\langle S' \Lambda' \Sigma' | H_{SO} | S'' \Lambda \Sigma'' \rangle}{\Delta E'} \right) \mu_{\Lambda \Sigma'' \Lambda'' \Sigma''}^{S'' S''} \right]. \end{aligned} \quad (33.89)$$

However, care must be taken in reducing these matrix elements using the Wigner–Eckart theorem, for example, following *Lefebvre-Brion* and *Field* [33.55], in order to satisfy the $\Delta\Omega = 0$ requirement for matrix elements of the rotationless Hamiltonian.

33.8.2 Orbitaly-Forbidden Transitions

Even if the upper and lower states share the same value of electron spin, the transition may still be forbidden. The change in orbital angular momentum may be too large, $|\Delta\Lambda| > 1$, or a change in reflection parity, $\Sigma^- \rightarrow \Sigma^+$, may cause the zero-order transition matrix elements to vanish. Spin-orbit mixing with other $2S+1\Lambda$ states, as described above, is usually the largest source of transition probability. In addition, terms in the Hamiltonian of the form $\mathbf{J} \cdot \mathbf{L}$ lead to contributions to the transition strength that increase with J , and that may mix-in higher values of Ω than were present in

the zero-order $\Lambda\Sigma$ basis set for the upper and lower states. This situation can be represented by generalizing the formula from Sect. 33.7.2, following *Huestis* et al. [33.23],

$$\begin{aligned} S_{J' J''}^{c' c''} &= \left| \sum_{K' K''} b_{J' c'}^{* K'} a_{J'' c''}^{K''} \right. \\ & \quad \left. \times \sum_{i=-1}^1 \mu_{K' K''}^{(i)} \zeta^{(i)}(J', K', J'', K'') \right|^2, \end{aligned} \quad (33.90)$$

where $\mu_{K' K''}^{(0)}$ is the rotationless contribution ($\mu_{K' K''}^{(\pm 1)}$ from Sect. 33.7.2) and $\mu_{K' K''}^{(\pm 1)}$ are the new rotation-assisted terms. The new reflection-symmetry rule is

$$\mu_{-K' - K''}^{(i)} = \eta(-1)^{K' - K'' + i} \mu_{K' K''}^{(-i)}. \quad (33.91)$$

The revised square-root Hönl–London factors are

$$\zeta^{(0)}(J', K', J'', K'') = \zeta(J', K', J'', K'') \quad (33.92)$$

(from Sect. 33.7.2) and

$$\begin{aligned} & \zeta^{(\pm 1)}(J', K', J'', K'') \\ &= \frac{1}{2} \left\{ [J'(J'+1) - K'(K' \mp 1)]^{1/2} \right. \\ & \quad \times \zeta(J', K' \mp 1, J'', K'') \\ & \quad \left. + [J''(J''+1) - K''(K'' \pm 1)]^{1/2} \right. \\ & \quad \left. \times \zeta(J', K', J'', K'' \pm 1) \right\}. \end{aligned} \quad (33.93)$$

As in Sect. 33.7.2 the symbols K' and K'' represent $\Lambda' \Sigma'$ and $\Lambda'' \Sigma''$ when used as labels, and Ω' and Ω'' when used as numbers (a distinction that is relevant only when $S \geq |\Lambda|$ and $\Lambda \neq 0$). This formulation is more symmetric than that proposed by *Huestis* et al. [33.23], in that it explicitly allows for either the upper or lower state to be mixed by rotation (of significance only for low J and $\Delta\Lambda > 1$).

33.9 Recent Developments

Added by Mark M. Cassar. Astronomical sky spectra are important for an understanding of processes both in Earth's and other terrestrial environments. These spectra are the background spectra obtained through the slit of a spectrometer while excluding the object of primary interest to the astronomer – the star, galaxy, etc. The sky spectrum is subsequently subtracted from the object spectrum so that the final product contains no emis-

sions from extraneous sources – nightglow, zodiacal light, and the light of other stellar objects. This operation then leaves the astronomer with purer astronomical spectra, which can then be compared to theoretical transition probability calculations to identify emission sources. This procedure has recently been used to identify the atomic oxygen green line in the Venus night airglow [33.77], which relied on an understanding of

molecular oxygen emissions. In addition, interpretation of the intensities of molecular oxygen emissions also furthers the understanding of the elementary processes occurring in the Earth's atmosphere [33.78].

Two recent studies have focused on the radiative properties of the CaN and $^{39}\text{K}^{85}\text{Rb}$ molecules. In the former study, the radiative transition probabilities and lifetimes for the $A^4\Pi - X^4\Sigma^-$ and $B^4\Sigma^- - X^4\Sigma^-$ band systems were calculated [33.79]. These results will in turn facilitate future spectroscopic studies of CaN showing the essential interplay between theory and experiment, which is required for a deeper un-

derstanding of these processes. (Radiative properties are sensitive to electronic coupling schemes and to configuration interaction, and thus present an important testing ground for theoretical models [33.80, 81].) The second study provides quantitative estimates for the radiative cooling of heteronuclear translationally ultracold molecules [33.82, 83]. By calculating the radiative transition probabilities for $^{39}\text{K}^{85}\text{Rb}$, which lead to the radiative lifetime through the total Einstein A coefficient, it has been shown that under appropriate laboratory conditions such a cooling process is not relevant [33.84].

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