

N08600017

UNIVERSITY OF OSLO



INSTITUTE OF PHYSICS

REPORT SERIES

SYMMETRIES AND ROTATIONAL LINE INTENSITIES
IN DIATOMIC MOLECULES.

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Report 86-05

Received 27/02-1986

ABSTRACT

The general theory of angular momenta and the full rotation group is used to reconsider the theory of the intensity factors of rotational lines in the spectra of diatomic molecules (Hönl-London factors). No familiarity with group theory is, however, expected from the reader, as the rather few new concepts introduced are fully explained. It is shown that the use of the rotational symmetry (rotation matrices) leads to compact and elegant derivations of the symmetry properties of the molecular wave functions, as well as the matrix elements of the transition operator. The present work is restricted to spin-allowed electric dipole transitions, and the general sum rule characteristic of this type of transitions, is rederived in an easy way by use of the general angular momentum theory.

A main purpose of the present work has been to provide a unified theoretical basis for exact numerical computations of Hönl-London factors for all types of spin-allowed electric dipole transitions in diatomic molecules. The computed Hönl-London factors are then in the next step intended to be the basis for construction of synthetic molecular band spectra, with particular applications to upper atmospheric emissions (aurora).

1. INTRODUCTION

Rotational spectra of diatomic molecules are encountered in a great variety of circumstances, from the high precision microwave or laser studies of chemical and physical spectroscopy laboratories, to the rather unresolved optical spectra of astrophysical and upper atmospheric sources.

The quantum theory of the rotational-line intensities in diatomic molecules dates back to the paper of Hönl and London from 1925(1). Hönl and London derived the rotational-intensity factors (Hönl-London factors) for the simple singlet-singlet electronic transitions. Since that time, analytic expressions for rotational-intensity factors have been derived for most relevant electronic transitions of diatomic molecules, and comprehensive tabulations of the results are given in the book by Kovacs (2). However, many of the analytic expressions are based on approximations of different kinds, and more than 10 years ago the first computer codes were written to produce exact numerical rotational-line intensity factors (Whiting (3), Zare (4)). The analytic formulae are none the less still in common use, also in spite of the fact that they are quite complex in most cases, actually requiring their own computer codes to be written.

The present theoretical investigation of the intensities of diatomic rotational lines is part of a program that has been started to produce synthetic rotational spectra for use in the study of upper atmospheric emissions. The first emission to be considered was the $O_2^+ b^1\Sigma_g^- - a^1\Pi_g$ transition (1st negative bands). Existing analytic intensity factors for this very complex spectrum are approximations, based on limiting models (Hund's cases (b) and (a)) of the angular momentum coupling. Hence, it was realized that the synthetic spectrum had to be based on exact

numerical intensity factors. That procedure, however, led to a deeper involvement in the theory, with subsequent reflections on how to derive the formulae required in the most efficient way. In the course of this work the idea then emerged that the theory of rotational-line intensities could be formulated in a compact and elegant manner by use of the well-established theory of the full rotation group. Furthermore, it also turned out that familiarity with group theory would actually not be required to follow the derivations. Hence, the present approach enables a central part of molecular physics to be reformulated in a language that is common to other important branches of physics, e.g. atomic and nuclear physics.

Much attention is in the first part of the paper given to the study of the molecular eigenstates. The rotational part of the molecular wave function is related to the rotation matrices, which in an easy way exhibit the important properties of the wave function. Emphasis is also put on discussing the molecular basis sets known as Hund's coupling cases (a) and (b), and how these two complete sets of molecular angular momentum eigenstates are related. Here again, the use of the rotational symmetry (the rotation matrices) yields simple and elegant derivations, and it is the hope of the author that the present approach may help to de-mystify the angular momentum coupling models, as well as the transformation from one model to the other.

The present work is not intended to be a survey paper, which means that a comprehensive list of references will not be provided. A few works of particular importance for the present investigation will, however, be cited in the introduction. In chronological order these are: The monograph by Hougen (5), the paper by Zare et al. (6), which yields useful information on the

molecular Hamiltonian, and on the inversion symmetry of the molecular states, the reinvestigation of the rotational-line intensity factors by Whiting and Nicholls (7), and the paper by Brown and Howard (8), who discussed the transformation between coupled and decoupled basis sets in terms of the rotation matrices.

Finally, the important books on the theory of angular momenta by Edmonds (9), and by Brink and Satchler (10) are basic sources for the present work.

2. TRANSITION PROBABILITY AND LINE STRENGTH

We shall start by giving the transition probability (transition rate per particle) for a spontaneous radiative transition from an upper rotational level J' of a molecular system to a lower rotational level J'' . The expression for the transition probability $A_{J',J''}$ is (11):

$$A_{J',J''} = \frac{64 \pi^4 e^2 a_0^2}{3 h} \nu_{J',J''}^3 \frac{S_{J',J''}}{(2J'+1)}, \quad (1)$$

where $\nu_{J',J''}$ denotes the energy difference $E_{J'} - E_{J''}$ in wave numbers (cm^{-1}). The line strength $S_{J',J''}$ is defined by

$$S_{J',J''} = \sum_{M',M''} |\langle \Psi_{J',M'} | \mu | \Psi_{J'',M''} \rangle|^2, \quad (2)$$

and this is the quantity on which our attention will be focused in the present investigation. In equation (2) $\Psi_{J',M'}$ and $\Psi_{J'',M''}$

denote the total molecular wave function for upper and lower states respectively, and the quantum numbers M' and M'' are associated with the space fixed Z-component of the total angular momentum \underline{J} . The remaining quantum numbers needed to completely specify the molecular states will be suppressed at this stage of the development. Finally, $\underline{\mu}$ is the total transition operator

$$\underline{\mu} = \underline{i} \mu_x + \underline{j} \mu_y + \underline{k} \mu_z \quad , \quad (3)$$

and only electric dipole transitions will be considered in the present work. The radiation described by eqs. (1) and (2) is isotropic and unpolarized (Condon and Shortley(12), p. 99).

Inserting eq. (3) in eq. (2) one obtains

$$S_{J'J''} = \sum_{M', M''} \left\{ \left| \langle \Psi_{J'M'} | \mu_x | \Psi_{J''M''} \rangle \right|^2 + \left| \langle \Psi_{J'M'} | \mu_y | \Psi_{J''M''} \rangle \right|^2 + \left| \langle \Psi_{J'M'} | \mu_z | \Psi_{J''M''} \rangle \right|^2 \right\} \quad , \quad (4)$$

and it is rather straightforward to show that the three summations in eq. (4) will all yield the same result (Condon and Shortley (12), p. 72), i.e.

$$S_{J'J''} = 3 \sum_{M', M''} \left| \langle \Psi_{J'M'} | \mu_z | \Psi_{J''M''} \rangle \right|^2 \quad . \quad (5)$$

Here we have retained the Z-component of the transition operator, which yields the simplest expressions for further calculations. An outline of the derivation of eq. (5) from eq. (4) will now be given. The derivation of eq. (5) is best carried out by introdu-

cing some new terminology which is normally not used in the theory of diatomic intensities. First the spherical components of the transition moment are defined by

$$\mu_{\pm 1} = \mp \frac{1}{\sqrt{2}} (\mu_x \pm i\mu_y) \quad (6)$$

$$\mu_0 = \mu_z$$

The cartesian components of $\underline{\mu}$ are now expressed in terms of the spherical ones, and the Wigner-Eckart theorem (9,10) yields the following expression for the matrix elements of the transition operators needed in eq. (4):

$$\langle \bar{\Psi}_{J'M'} | \mu_m | \bar{\Psi}_{J''M''} \rangle = (-1)^{M'+J''-1} (J' || \mu || J'') \times (2J'+1)^{1/2} \begin{pmatrix} J'' & 1 & J' \\ M'' & m & -M' \end{pmatrix} \quad (7)$$

Here $(J' || \mu || J'')$ denotes the reduced matrix element of the transition operator (independent of M' and M''), m designates the spherical components of $\underline{\mu}$ ($m = 0, \pm 1$), and a few important properties of the $3j$ -symbol are given in the appendix. Eq. (5) is now easily derived from eq. (4) by use of eq. (7), and a simple orthogonality relation of the $3j$ -symbols given in the appendix.

3. THE MOLECULAR WAVE FUNCTION

To further develop the expression for the line-strength of Eq. (5) we now need more explicit expressions for the molecular

wave functions. The point of departure for molecular quantum mechanical calculations is the Born-Oppenheimer approximation. The total molecular Hamiltonian H may be partitioned as

$$H = H_{ev} + H_{rot} \quad , \quad (8)$$

where H_{ev} depends on electronic and vibrational variables only, whereas the "rotational" part H_{rot} unfortunately also contains electronic and vibrational variables. Suppressing the electronic and vibrational dependence of H_{rot} yields the molecular wave function in the Born-Oppenheimer approximation

$$\Psi = \Psi_{ev} \Psi_{rot} \quad , \quad (9)$$

where Ψ_{ev} represents the electronic- and vibrational wave function for a non-rotating molecule, and Ψ_{rot} is the rotational wave function of a rigid rotator. Now, the Born-Oppenheimer type of wave functions span a complete set, and a "true" molecular wave function may eventually be obtained from perturbation theory in terms of an expansion in Born-Oppenheimer functions.

Further specification of the electronic and vibrational (vibronic) wave function Ψ_{ev} and the rotational wave function Ψ_{rot} of eq. (9) is now needed. The present investigation will be restricted to diatomic molecules only. The vibronic wave function is then characterized by the vibrational quantum number v , by the quantized component (Λ) of the electronic orbital angular momentum along the internuclear axis, and by the total electronic spin quantum numbers S and M_S . Note that the electronic spin is assumed to be quantized (M_S) along a space fixed axis. Further-

more, the vibronic wave function may be separated into a vibrational part and an electronic part

$$\Psi_{ev}(r, \underline{q}) = \Psi_{nr}(r) \Psi_{n\Lambda S M_S}(r, \underline{q}), \quad (10)$$

where n is a label (extra quantum numbers) needed to differentiate between electronic states with the same set of quantum numbers Λ and S . q denotes the whole body of electronic coordinates, including spin-coordinates, and r is the internuclear separation.

The rigid rotator wave function Ψ_{rot} of Eq. (9) is specified by the quantum members N , M_N , and Λ . The quantum numbers N and M_N correspond to the quantized values of \underline{N}^2 and N_z (space-fixed Z -component), where \underline{N} is the total molecular angular momentum except for spin. In this way the total molecular wave function is characterized by five angular momentum quantum numbers, i.e. Λ , S , M_S , N , and M_N , corresponding to mutually commuting operators. Now, we can also see the reason why the electronic spin had to be quantized along a space-fixed axis in eq. (10), the molecule-fixed components of \underline{S} do not commute with the components of \underline{N} , which rotates the molecular frame of reference.

A rotating diatomic molecule is obviously a symmetric top. The problem is, however, that for diatomic or linear molecules the rotation around the molecular axis is undefined, so that the known wave function for a symmetric top which depends on the complete set of three Eulerian angles, can not be used right away. This problem has, however, been considered by Hougen (13), who concludes that the standard expression for the wave function of a symmetric top can be used for a linear molecule as well, provided that the Eulerian angle describing rotation around the

molecular axis is discarded, i.e. set equal to zero.

The rotational wave function of a diatomic molecule is then most conveniently given as (Brink and Satchler (10))

$$\bar{\Psi}_{N M_N \Lambda}(\varphi, \theta) = \left[\frac{2N+1}{4\pi} \right]^{1/2} D_{M_N \Lambda}^{(N)}(\varphi, \theta, 0)^* \quad (11)$$

where the square root represents a normalization factor, and the D-symbols are elements of the so called rotation matrices. Further properties and definitions of the rotation matrices are given in the appendix. The angles θ and φ of eq (11) are now the two Eulerian angles needed to specify the orientation of the molecular axis in a space-fixed system, cf. fig. 1.

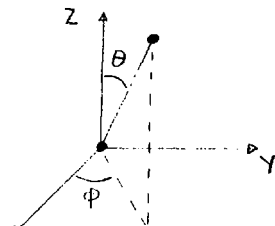


Fig. 1.

In the bra-ket notation the Born-Oppenheimer wave function may now finally be written:

$$|n \nu \Lambda S N M_S M_N \rangle = |n \nu \rangle |n \Lambda S M_S \rangle |N M_N \Lambda \rangle \quad (12)$$

4. HUND'S COUPLING CASES (a) AND (b)

The uncoupled molecular states represented by eq. (12), in which the electronic spin as well as the total angular momentum except for spin are quantized along the space-fixed Z-axis, are not the most convenient basis states for molecular calculations. A better basis set which also conforms more closely to the

physical reality is obtained by adding \underline{S} and \underline{N} to a total angular momentum \underline{J} in the standard way (8)

$$|n \nu \Lambda S N J M_J\rangle = (-1)^{N-S+M_J} (2J+1)^{1/2} \quad (13)$$

$$\times \sum_{M_N, M_S} \begin{pmatrix} N & S & J \\ M_N & M_S & -M_J \end{pmatrix} |n \nu\rangle |n \Lambda S M_S\rangle |N M_N \Lambda\rangle,$$

where the addition of the angular momenta is expressed in terms of the $3j$ -symbols (see appendix), rather than in terms of the more unsymmetric Clebsch-Gordan coefficients. The coupled molecular state of eq. (13) with quantum numbers Λ , S , N , J , and M_J (corresponding to J_z) is known as Hund's coupling case (b).

Molecular basis states in which the electronic spin is quantized along the molecular axis are, however, more convenient for most applications. This type of basis states are denoted Hund's coupling case (a). A relation between coupling cases (a) and (b) can be obtained from eq. (13) by recoupling the right-hand side angular momenta (8).

The electronic state $|n \Lambda S M_S\rangle$ is expanded in terms of molecule-fixed spin states $|n \Lambda S \Sigma\rangle$ as follows:

$$|n \Lambda S M_S\rangle = \sum_{\Sigma} D_{M_S \Sigma}^{(S)}(\phi, \theta, 0)^* |n \Lambda S \Sigma\rangle, \quad (14)$$

where the rotation matrices (cf. appendix) are used to rotate the spin states. Inserting eq. (14) in eq. (13), using eq. (11) for the rotational wave function, and coupling together the two rotational matrices according to equation (a5) of the appendix, we finally obtain for the case (b) wave function (8)

$$\Psi_{n \nu \Lambda N S J M_J} = [(2J+1)(2N+1)/4\pi]^{1/2} \quad (15)$$

$$\times \sum_{\Sigma, \Omega} (-1)^{-J-\Omega} \begin{pmatrix} N & S & J \\ -\Lambda & -\Sigma & \Omega \end{pmatrix} D_{M_J \Omega}^{(J)}(\phi, \theta, 0)^* \Psi_{n \nu \Lambda S \Sigma},$$

with $\Omega = \Lambda + \Sigma$. From eq. (15) we now see that the rotation matrix $D^{(J)}_{M_3, \Omega}(\varphi, \theta, 0)^*$ acts as an eigenfunction for the total angular momentum squared $\underline{J}^2 = (\underline{N} + \underline{S})^2$, and for J_z . This conclusion is particularly interesting in view of the fact that J may be half-integral. Introducing the rotational state $|JM_3\Omega\rangle$ in analogy with eq. (11) we then have the following relation between the case (b) and case (a) basis states:

$$|n\nu\Lambda NSJM_3\rangle = (2N+1)^{1/2} \sum_{\Sigma, \Omega} (-1)^{-J-\Omega} \begin{pmatrix} N & S & J \\ -\Lambda & -\Sigma & \Omega \end{pmatrix} |n\nu\Lambda S\Sigma JM_3\rangle, \quad (16)$$

or inverted

$$|n\nu\Lambda S\Sigma JM_3\rangle = \sum_N (-1)^{J+\Omega} (2N+1)^{1/2} \begin{pmatrix} J & N & S \\ \Omega & -\Lambda & -\Sigma \end{pmatrix} |n\nu\Lambda NSJM_3\rangle.$$

The last of eqs. (16) above now gives the case (a) basis states in terms of the case (b) states, and via eq. (13) also in terms of the basic uncoupled states $|n\nu\Lambda SM_3 NM_3\rangle$. This relation will be very useful for exploring the symmetry properties of the case (a) states.

5. SYMMETRIES OF THE MOLECULAR WAVE FUNCTIONS.

The selection rules in molecular spectra are governed by the symmetry properties of the molecular wave function. In a diatomic molecule there are two important geometrical symmetry operations which we shall now consider. The first one is reflection of all the molecule-fixed electronic coordinates in a plane containing the molecular axis, this operation is normally denoted σ_v . The operation σ_v obviously affects only the electronic part of the wave function, which in the language of group theory forms a

basis for one-dimensional ($\Lambda = 0$) irreducible representations of the diatomic symmetry group $C_{\infty v}$. Hence, we may write (cf. eqs. (12-13))

$$\sigma_v |n \Lambda S M_S\rangle = (-1)^{\Lambda n} |n -\Lambda S M_S\rangle. \quad (17)$$

For $\Lambda = 0$ there are two distinct one-dimensional representations for $C_{\infty v}$, the one Σ^+ corresponding to a phase factor $+1$ in eq. (17), and the other Σ^- corresponds to a phase factor -1 in eq. (17). Each value of $\Lambda \neq 0$ corresponds to just one two-dimensional irreducible representation of $C_{\infty v}$, and we are at liberty to choose the phase factor of eq. (17) equal to $+1$ in all cases with $\Lambda \neq 0$.

The second and most important geometric symmetry operation in a diatomic molecule is inversion, which means inversion of the coordinates of all particles (electrons and nuclei) in a space-fixed frame of reference. The inversion operation which is normally denoted I , may be carried out in two steps according to the equation (Zare et al. (6))

$$I = C_2^* \sigma_v^{yz} \quad (18)$$

Here σ_v^{yz} means reflection of the electronic coordinates in the yz -plane of the molecule-fixed coordinate system, and C_2^* is a rotation of the molecule-fixed coordinate system an angle Π around the molecule-fixed x -axis.

The operation C_2^* only affects the Euler angles describing the orientation of the molecular axis, and hence only the rotational part $|NM\Lambda\rangle$ (cf. eqs. (11-13)) of the molecular state. The operation C_2^* is carried out by the substitution (Zare et al. (6))

$$\varphi \rightarrow \varphi + \pi$$

$$\theta \rightarrow \pi - \theta$$

in the angles of eq. (11). From the properties of the rotational matrices (cf. appendix) it is then straightforward to show that

$$C_2^x |N M_N \Lambda\rangle = (-1)^N |N M_N -\Lambda\rangle. \quad (19)$$

The action of the inversion operator I on the whole decoupled molecular state eq. (12) is then easily obtained by use of eqs. (17-19)

$$I |n \nu \Lambda S N M_S M_N\rangle = (-1)^{N+\Lambda_n} |n \nu -\Lambda S N M_S M_N\rangle. \quad (20)$$

The effect of I on the case (b) states is then straightforward from eq. (13)

$$I |n \nu \Lambda S N J M_J\rangle = (-1)^{N+\Lambda_n} |n \nu -\Lambda S N J M_J\rangle. \quad (21)$$

In eqs. (20-21) it is again recalled that $s_n = 1$ for Σ^- states, and that $s_n = 0$ may be chosen for all other electronic states.

Our interest is, however, primarily concerned with the inversion property of the more complex case (a) states. From eq. (21) and the last of eqs. (16) it now follows after a little piece of algebra that

$$I |n \nu \Lambda S \Sigma J M_J\rangle = (-1)^{J-S+\Lambda_n} |n \nu -\Lambda S -\Sigma J M_J\rangle, \quad (22)$$

in agreement with the results of previous investigations (14).

However, the phase factor of eq. (22) do not agree with the result of Zare et al. (6). There seems to be an inconsistency in

the way eq. (A19) of Zare et al. (6) is derived from their eqs. (A12) and (A18). In eq. (A18) it seems to be overlooked that there is no complex conjugation of the rotation matrix, and the present author obtained the phase factor $(-1)^{-M}$ in eq. (A19) of Zare et al., instead of their factor $(-1)^M$. This distinction is obviously of importance for half-integral values of S .

From eqs. (21-22) it is clear that neither the case (a) states nor the case (b) states are eigenstates of the inversion operator I . Simple linear combinations of the two states degenerate in Λ , however, yield eigenstates of I , e.g. for the case (a) states

$$|\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}} \left(|n v \Lambda S \Sigma J M_J\rangle \pm (-1)^{J-S+\Lambda_n} |n v -\Lambda S -\Sigma J M_J\rangle \right). \quad (23)$$

The phase factor $(-1)^{J-S+\Lambda_n}$ of eq. (23) is normally omitted when inversion eigenstates are constructed. Inclusion of this phase factor, however, ensures that the upper sign in eq. (23) will always correspond to the inversion eigenvalue (parity) $+1$, and the lower sign to parity -1 . This detail simplifies the book-keeping in perturbation - and intensity calculations.

For a homonuclear diatomic molecule there are two additional geometric symmetry operations that will be commented on. The first one is the inversion (i) of all the molecule-fixed electronic coordinates. For a homonuclear diatomic molecule the symmetry group is $D_{\infty h}$ and the effect of the operation i on the electronic state is

$$i |n v \Lambda S M_S\rangle = (-1)^{i_n} |n v \Lambda S M_S\rangle, \quad (24)$$

where $i_n = 0$ for g (gerade) electronic states, and $i_n = 1$ for u (ungerade) states.

The second symmetry operation is the permutation (P) of the identical nuclei. The following relation applies (Haugen (5))

$$P = I \cdot i \quad (25)$$

To investigate the properties of the permutation operator P we would have to include the nuclear spin in the molecular wave function, a topic which falls outside the scope of the present investigation (see for instance Herzberg (15)). For homonuclear diatomic intensity calculations it is, however, important to bear in mind that the influence of the nuclear spin leads to intensity alternations due to different weight factors of the individual rotational levels. As long as the hyperfine structure is unresolved, there is no influence of the nuclear spin on the intensities of the lines of heteronuclear systems.

6. TIME REVERSAL

The behaviour of the molecular states under time reversal yields information which is useful for the computation of molecular intensities. The time reversal operator is for a n-electron system given by (Wigner (16)):

$$T = \sigma_{1y} \sigma_{2y} \dots \sigma_{ny} K \quad , \quad (26)$$

where $\sigma_{1y}, \dots, \sigma_{ny}$ are the Pauli spin matrices, and K is complex conjugation.

The effect of the time reversal operator is most easily obtained for the uncoupled states of eq. (12), and thereafter for the case (b) and case (a) states by use of eqs. (13) and (16). For the spin-independent rotational state $|NM_M \Lambda\rangle$ of eq. (12) the

effect of T is simply complex conjugation, and from eq. (11) we have

$$T |N M_N \Lambda\rangle = (-1)^{\Lambda - M_N} |N - M_N - \Lambda\rangle \quad (27)$$

by use of the relation (a3) for the rotational matrices (cf. appendix). Since the case (a) rotational state $|JM_J\Omega\rangle$ is defined in complete analogy with eq. (11) (cf. eq. (15)) we also have

$$T |J M_J \Omega\rangle = (-1)^{\Omega - M_J} |J - M_J - \Omega\rangle. \quad (28)$$

To obtain the time reversal properties of the electronic state $|n\Lambda S M_S\rangle$ requires a little more effort. It is convenient to write the electronic wave function as an antisymmetric product of one-electron orbital (ψ_i) and spin (χ_i) functions:

$$\Psi_{n\Lambda S M_S} = \mathcal{A} \psi_1 \psi_2 \cdots \psi_n \chi_1 \chi_2 \cdots \chi_n, \quad (29)$$

where \mathcal{A} is the antisymmetrizer,

$$\mathcal{A} = \frac{1}{\sqrt{n!}} \sum_P (-1)^P P. \quad (30)$$

Here the summation runs over all the permutations P of the n electrons, and p is the number of binary permutations in the permutation P . From eqs. (26) and (30) we deduce $[T, \mathcal{A}] = 0$, hence

$$T \Psi_{n\Lambda S M_S} = \mathcal{A} \psi_1^* \psi_2^* \cdots \psi_n^* T(\chi_1 \chi_2 \cdots \chi_n).$$

Now from eq. (26)

$$T(\chi_1 \chi_2 \cdots \chi_n) = (-i)^{2M_S} \chi_1^- \chi_2^- \cdots \chi_n^-, \quad (31)$$

where the minus on the spin-functions indicates that the spin has been reversed.

The space orbitals may be represented by a linear combination of atomic orbitals on the two nuclei ($\alpha = 1, 2$)

$$\psi_{\lambda_i} = \sum_{\ell \geq |\lambda_i|} \sum_{\alpha=1}^2 c_{\ell\alpha}(r_\alpha) Y_{\ell\lambda_i}(\theta_\alpha, \phi_\alpha), \quad (32)$$

where λ_i refers to the quantized component of the one-electron orbital angular momentum along the molecular axis. Since the radial factors of eq. (32) may all be chosen real, we have

$$\psi_{\lambda_i}^* = (-1)^{\lambda_i} \psi_{-\lambda_i}.$$

In conclusion we then have for the electronic state

$$T|n \Lambda S M_S\rangle = (-1)^{\Lambda+M_S} |n - \Lambda S - M_S\rangle. \quad (33)$$

In the most general case we may have to represent the electronic wave function by a linear combination of antisymmetric products (cf. eq. (29)). However, all products will have the same value of Λ and M_S , and eq. (33) is unaffected.

From eqs. (13), (27), and (33) we then obtain for the case (b) states after a little algebra

$$T|n \nu \Lambda S N J M_J\rangle = (-1)^{J-S-N+M_J} |n \nu - \Lambda S N J - M_J\rangle. \quad (34)$$

Finally, the time reversal of the case (a) states is determined by eq. (16):

$$T|n \nu \Lambda S \Sigma J M_J \Omega\rangle = (-1)^{M_J} |n \nu - \Lambda S - \Sigma J - M_J - \Omega\rangle. \quad (35)$$

Different phase conventions seem to be in use regarding the time reversal of spin states. The present result of eq. (28) for the time reversal of the case (a) rotational state is in agreement

with the results of Hougen (5) for integral as well as half-integral values of J.

A quicker derivation of eq. (35) is obtained by noticing that eq. (31) applies as well to spins quantized in the molecule-fixed system (along the molecular axis), we just have to replace M_s by Σ . In analogy with eq. (33) we then have for the case (a) electronic state

$$T|n\Lambda S\Sigma\rangle = (-1)^{\Lambda+\Sigma} |n-\Lambda S-\Sigma\rangle, \quad (36)$$

and eq. (35) follows by use of eq. (28).

The vibrational wave functions of a diatomic molecule are real, and accordingly invariant under time reversal.

7. MATRIX ELEMENTS OF THE TRANSITION OPERATOR.

We are now ready to return to the line strength of eq. (5) and compute the matrix elements of the space-fixed Z-component of the transition operator. The "true" molecular state may be expressed in terms of a linear combination of coupling case (a) or case (b) basis states (cf. next section). Hence, we only need to compute the matrix elements of μ_z within a given basis set. The coupling case (a) basis set is most frequently used for diatomic calculations, and that will also be our present choice.

The inversion symmetry or parity plays an important role in radiative transitions, and we shall start from the parity eigenstates of eq. (23). Hence, we consider

$$\begin{aligned} \langle \Psi_{\pm}^{\prime} | \mu_z | \Psi_{\mp}^{\prime\prime} \rangle &= \langle n^{\prime} v^{\prime} \Lambda^{\prime} S^{\prime} \Sigma^{\prime} J^{\prime} M_J^{\prime} | \mu_z | n^{\prime\prime} v^{\prime\prime} \Lambda^{\prime\prime} S^{\prime\prime} \Sigma^{\prime\prime} J^{\prime\prime} M_J^{\prime\prime} \rangle \\ &+ (-1)^{J^{\prime\prime} - S^{\prime\prime} + \Lambda^{\prime\prime}} \langle n^{\prime} v^{\prime} \Lambda^{\prime} S^{\prime} \Sigma^{\prime} J^{\prime} M_J^{\prime} | \mu_z | n^{\prime\prime} v^{\prime\prime} - \Lambda^{\prime\prime} S^{\prime\prime} - \Sigma^{\prime\prime} J^{\prime\prime} M_J^{\prime\prime} \rangle, \end{aligned} \quad (37)$$

where we have used the inversion symmetry ($I^2 = 1$), eq. (22), and the fact that the components of the electric dipole transition operator changes sign under inversion. Eq. (37) also reflects the fact that electric dipole transitions are allowed only between states of opposite parity.

In its general form eq. (37) applies only for $\Lambda' \neq 0$ and $\Lambda'' \neq 0$. For a state with $\Lambda = 0$ the corresponding Σ quantum numbers must be positive or zero (cf. eq. (23)). In the case of $\Lambda' = \Lambda'' = \Sigma' = \Sigma'' = 0$ there is obviously a contribution only from the first term on the right-hand side in eq. (37). Furthermore, if $\Lambda' \neq 0$ and $\Lambda'' = \Sigma'' = 0$ (or $\Lambda'' \neq 0$, $\Lambda' = \Sigma' = 0$) then the right-hand side of eq. (37) has to be multiplied by the factor $1/\sqrt{2}$.

The next step in the evaluation of eq. (37) is to transform the space-fixed component of the dipole operator to a molecule-fixed system. This step is necessary to cope with the electronic wave functions which are given in a molecule-fixed system. This transformation is normally carried out by use of the direction cosines. However, the rotation matrices yield a more convenient transformation. The following relation applies:

$$\mu_z = \sum_m D_{0m}^{(1)}(\varphi, \theta, 0)^* \mu_m, \quad (38)$$

where μ_m ($m = 0, \pm 1$) now denotes the molecule-fixed spherical components of $\underline{\mu}$ (cf. eq. (6)).

By use of eqs. (a3) and (a6) of the appendix a general matrix element of the type needed in eq. (37) is then obtained as (cf. eq. (15))

$$\begin{aligned} & \langle n'v'\Lambda'S'\Sigma'J'M_J' | \mu_z | n''v''\Lambda''S''\Sigma''J''M_J'' \rangle \\ & = \sum_m \langle n'v'\Lambda'S'\Sigma' | \mu_m | n''v''\Lambda''S''\Sigma'' \rangle \\ & \times (-1)^{M_J'' - \Omega'' - m} [(2J'+1)(2J''+1)]^{1/2} \begin{pmatrix} J' & 1 & J'' \\ \Omega' & -m & -\Omega'' \end{pmatrix} \begin{pmatrix} J' & 1 & J'' \\ M_J' & 0 & -M_J'' \end{pmatrix}. \end{aligned} \quad (39)$$

There are several important conclusions that follow immediately from eq. (39). From the properties of the $3j$ -symbols (cf. appendix) we have

$$\begin{aligned} J'' &= J', J' \pm 1 \\ M_J'' &= M_J' \\ \Omega'' &= \Omega' - m \end{aligned} \quad (40)$$

as general requirements for a non-zero matrix element. Since the electric dipole operator is independent of spin, we must also have $S'' = S'$ and $\Sigma'' = \Sigma'$. In view of eq. (40) this restriction leads to

$$\Lambda'' = \Lambda' - m, \quad (41)$$

which means that for given values of Λ' and Λ'' just one term in the summation over m will contribute in eq. (39). Hence, we see that the introduction of the spherical components of the transition operator leads to a very compact and informative expression for its matrix elements.

For $\Sigma = \Sigma$ electronic transitions ($\Lambda' = \Lambda'' = 0$) the reflection symmetry σ_v is also of interest. Since σ_v only acts on the molecule-fixed electronic coordinates we have for the case (a) electronic state in analogy with eq. (17)

$$\sigma_v |n \Lambda S \Sigma\rangle = (-1)^{\Lambda_n} |n - \Lambda S \Sigma\rangle,$$

and for the transition operator

$$\sigma_v^{y2} \mu_m (\sigma_v^{y2})^{-1} = \mu_{-m}.$$

Hence, we obtain

$$\begin{aligned} &\langle n' v' \Lambda' S \Sigma | \mu_m | n'' v'' \Lambda'' S \Sigma \rangle \\ &= (-1)^{\Lambda_n' + \Lambda_n''} \langle n' v' - \Lambda' S \Sigma | \mu_{-m} | n'' v'' - \Lambda'' S \Sigma \rangle. \end{aligned} \quad (42)$$

Now, for $\Lambda' = \Lambda'' = 0$ eq. (41) leads to $m = 0$, and non-zero matrix elements require that $s_{n'} + s_n$ is an even number, or in other words that both Σ states have to be of Σ^+ -type, or both of Σ^- -type.

For homonuclear molecules we also have to consider the effect of the inversion (i) of the molecule-fixed electronic coordinates (g-u symmetry). From eq. (24) and

$$i \mu_m i^{-1} = -\mu_m ,$$

we get the relation

$$\begin{aligned} & \langle n' v' \Lambda' S \Sigma | \mu_m | n'' v'' \Lambda'' S \Sigma \rangle \\ & = (-1)^{i_{n'} + i_{n''} + 1} \langle n' v' \Lambda' S \Sigma | \mu_m | n'' v'' \Lambda'' S \Sigma \rangle , \end{aligned} \quad (43)$$

and obviously non-zero matrix elements only between states of opposite g-u symmetry.

Finally, it is of interest to investigate whether a general matrix element of the transition operator is a real or a complex quantity. This question may be decided by invoking the time reversal symmetry (Hougen (5)). Application of the time reversal operator to the left-hand side of eq. (39) yields (cf. eq. (35))

$$\begin{aligned} & \langle n' v' \Lambda' S \Sigma J' M_J | \mu_z | n'' v'' \Lambda'' S \Sigma J'' M_J \rangle^* \\ & = \langle n' v' - \Lambda' S - \Sigma J' - M_J | \mu_z | n'' v'' - \Lambda'' S - \Sigma J'' - M_J \rangle \quad (44) \\ & = (-1)^{\lambda_{n'} + \lambda_{n''} + 1} \langle n' v' \Lambda' S \Sigma J' M_J | \mu_z | n'' v'' \Lambda'' S \Sigma J'' M_J \rangle , \end{aligned}$$

where the inversion operator I (cf. eq. (22)) has also been used for the last step in deriving eq. (44). Furthermore, the general expression of eq. (39) had to be used, together with the simple symmetry properties of the $3j$ -symbols (cf. appendix).

Now, eq. (44) clearly shows that the general matrix element of the transition operator is either a real or a purely imaginary quantity. Whether it is real or not do not depend on any of the angular momentum quantum numbers, but merely on the reflection symmetries of the two electronic states. In practice this means that all matrix elements of the transition operator may be considered real, as the imaginary unit will vanish in the expression for the line strength or transition probability (cf. eqs. (1) and (5)).

Since for given values of Λ' and Λ'' only one value of m will contribute to the summation in eq. (39), we also conclude that the electronic matrix elements of the molecule-fixed components of the transition operator are all either real or purely imaginary.

B. THE MOLECULAR EIGENSTATES

The molecular eigenstates are obtained in the form of expansions in terms of a complete set of basis states, e.g. the coupling case (a) basis set. To obtain the expansion coefficients we have to solve the molecular Schrödinger equation within the given basis set. This is a standard technique for solving quantum mechanical problems, and only a brief outline of the method is given here.

Our Hamiltonian may formally be written

$$H = H_{el} + H_{rot} + H_{spin} \quad , \quad (45)$$

which means that spin-dependent interactions (e.g. spin-orbit and spin-spin) have now been added to the Hamiltonian of eq. (8). A

general eigenstate of H may be written

$$|\Psi_{\gamma J M_J}\rangle = \sum_{n, \nu, \Lambda, S, \Sigma} \langle n \nu \Lambda S \Sigma J M_J | \Psi_{\gamma J M_J} \rangle |n \nu \Lambda S \Sigma J M_J\rangle, \quad (46)$$

as the eigenstates of H are also eigenstates of J^2 and J_z . γ denotes other quantum numbers (labels) needed to completely specify the rotational state.

In practice, however, the expansion in eq. (46) will be truncated so that n , ν , Λ , and S are kept at fixed values, and only Σ is allowed to run over its $2S+1$ values. This will normally be a completely legal approximation for the computation of intensities. Hence, within this approximation the expansion coefficients of eq. (46) are obtained by diagonalizing a $2S+1$ dimensional Hamiltonian matrix. In a more compact notation the eigenstates (expansion coefficients) are given by the column of the unitary matrix U determined by the relation

$$U^{-1} H U = D, \quad (47)$$

where the $2S+1$ eigenstates of H are the elements of the $2S+1$ dimensional diagonal matrix D.

In our further calculations it will be necessary to work with eigenstates of H that are also eigenstates of the inversion operator I (cf. eq. (23)). In a somewhat unsymmetric notation the eigenstate corresponding to the eigenvalue number k of H is then

$$|\Psi_{k n \nu \Lambda S \Sigma J M_J \pm}\rangle = \sum_{\Sigma} U_{\Sigma}(k) \frac{1}{\sqrt{2}} (|n \nu \Lambda S \Sigma J M_J\rangle \pm (-1)^{J-S+\Lambda_n} |n \nu -\Lambda S -\Sigma J M_J\rangle). \quad (48)$$

The phenomena of Λ -doubling of Π -states and ρ -doubling of Σ -states are not included in the theory if the eigenstates are truncated as in eq. (48). A Van Vleck transformation (cf. Zare et

al. (6)) may, however, be carried out to effectively include in the 2S+1 dimensional Hamiltonian matrix of eq. (47) the dominant corrections that are otherwise lost by the truncation as in eq. (48) (e.g. Λ -doubling and ρ -doubling).

The elements of the 2S+1 dimensional Hamiltonian matrix of eq. (47) are all well-known and tabulated (cf. table I of Zare et al. (6)).

We may now proceed to compute the elements of the transition operator μ_{\pm} between two rotational levels of two different vibronic states of a diatomic molecule. For Σ -states ($\Lambda = 0$) it is important to notice that we have to work with molecular states that are also eigenstates of the inversion-operator I (parity eigenstates). To obtain results of general validity, we accordingly have to base our calculations on parity eigenstates.

From eqs. (37), (39), and (48) we then derive the expression

$$\begin{aligned} & \langle \bar{\Psi}_{k''n''v''\Lambda''S''M_{J''}} | \mu_{\pm} | \bar{\Psi}_{k'nv\Lambda S M_J} \rangle \\ &= (-1)^{-\Lambda'} \langle n'v'\Lambda'S' | \mu_{\Lambda'-\Lambda''} | n''v''\Lambda''S'' \rangle [(2J'+1)(2J''+1)]^{1/2} \begin{pmatrix} J' & 1 & J'' \\ M_J & 0 & -M_{J''} \end{pmatrix} \\ & \times \left\{ \sum_{\Sigma} (-1)^{M_J - \Sigma} \alpha_{\Sigma}(k')^* \alpha_{\Sigma}(k'') \begin{pmatrix} J' & 1 & J'' \\ \Lambda'+\Sigma & -(\Lambda'-\Lambda'') & -\Lambda''-\Sigma \end{pmatrix} \right. \\ & \left. \mp (-1)^{J''-S+\Lambda''} \sum_{\Sigma} (-1)^{M_J - \Sigma} \alpha_{\Sigma}(k')^* \alpha_{-\Sigma}(k'') \begin{pmatrix} J' & 1 & J'' \\ \Lambda'+\Sigma & -(\Lambda'+\Lambda'') & \Lambda''-\Sigma \end{pmatrix} \right\}. \end{aligned} \quad (49)$$

In eq. (49) it is assumed that $\Lambda' \geq \Lambda''$, which represents no loss of generality. Since we work with parity eigenstates it follows that $\Lambda' \geq 0$ and $\Lambda'' \geq 0$. In the derivation of eq. (49) we have used the fact that the matrix elements of μ_m of eq. (39) are diagonal in Σ , and also independent of Σ . The latter conclusion follows easily from observing that $[\mu_m, S_{\pm}] = 0$, and $S_{\pm} |S \Sigma \rangle \sim |S \Sigma \pm 1 \rangle$ (molecule-fixed components of \mathcal{S}).

From eq. (49) it is also clear that the present

approximation (eq. (48)), an electric dipole transition between two vibronic states is completely described in terms of just one (real) matrix element of the molecule-fixed transition operator.

Another conclusion which is evident from eq. (49) is that there is a parity-dependent contribution to the matrix element of the transition operator only for $\Lambda' + \Lambda'' \leq 1$, i.e. only for $\Sigma - \Sigma$ or $\Pi - \Sigma$ transitions.

By the application of eq. (49) it is important to recall the comments made to the basic equation (37) regarding the special cases (special values of Λ and Σ).

9. THE LINE STRENGTH

The line strength for a transition between an upper state k', J' and a lower state k'', J'' is according to eqs. (5) and (49) given by

$$S_{k'J'k''J''} = 3 \sum_{M_3} \left| \langle \Psi_{k'n'\nu'\lambda'SJ'M_3} | \mu_z | \Psi_{k''n''\nu''\lambda''SJ''M_3} \rangle \right|^2$$

$$= 3 \left| \langle n'\nu'\lambda'S | \mu_{\lambda'-\lambda''} | n''\nu''\lambda''S \rangle \right|^2 (2J'+1)(2J''+1)$$

$$\times |f(k', k'', J', J'')|^2 \sum_{M_3} \begin{pmatrix} J' & 1 & J'' \\ M_3 & 0 & -M_3 \end{pmatrix}^2,$$

where $f(k', k'', J', J'')$ denotes the whole expression in the curly bracket in eq. (49). From the orthogonality relations of the $3j$ -symbols (cf. appendix) it follows that

$$\sum_{M_3} \begin{pmatrix} J' & 1 & J'' \\ M_3 & 0 & -M_3 \end{pmatrix}^2 = \frac{1}{3},$$

and we finally have

$$S_{k'j'k''j''} = \langle n'v'1'S | \mu_{k'-k''} | n''v''1''S \rangle^2 \mathcal{F}_{k'j'k''j''}^2, \quad (50)$$

when the Hönl-London factor $\mathcal{F}_{k'j'k''j''}$ is introduced for the rotational part of the line strength, i.e.

$$\mathcal{F}_{k'j'k''j''}^2 = (2j'+1)(2j''+1) |f(k', k'', j', j'')|^2. \quad (51)$$

There is an important comment that should be made to the line strength of eq. (50) or to the Hönl-London factor of eq. (51). If the quantity $|f(k', k'', j', j'')|^2$ is written out explicitly it would contain a typical factor of the form

$$u_{\pm}(k') u_{\pm}(k'')^* u_{\pm}(k')^* u_{\pm}(k''),$$

i.e. a very critical dependence on the expansion coefficients of the molecular state (cf. eq. (48)). Hence, it is important that exact numerical values of the expansion coefficients are used when the Hönl-London factors are computed. Traditionally analytic expressions for the expansion coefficients have been sought, so that analytic formulae could be obtained for the Hönl-London factors (Kovacs (2)). For multiplicities higher than 2 the analytic procedure inevitably leads to approximations, and the accuracy of the formulae will be difficult to estimate due to the complexity of the problem. Furthermore, with the analytic approach simplifications will also be required in the molecular Hamiltonian. Existing analytic formulae are normally based on the vibrating rotator model, plus an effective spin-orbit coupling Hamiltonian. In the numeric approach to the Hönl-London factors there are no problems involved in including corrections like centrifugal distortions or spin-spin interactions.

The labels k' and k'' used to identify the eigenvalues of the Hamiltonian, correspond to the standard term value designations

$F_{k'}$ and $F_{k''}$, respectively (Herzberg (15)). The correlation between the eigenvalues (the elements of the diagonal matrix D of eq. (47)) and the term value symbols is straightforward, as $k = 1$ corresponds to the lowest eigenvalue, and so on up to $k = 2S+1$.

Recalling the separability of the vibronic wave function into a vibrational and an electronic part (eq. (10)), we have for the vibronic part of the line strength of eq. (50):

$$\begin{aligned} & |\langle n'v'\lambda'S | \mu_{\lambda'\lambda''} | n''v''\lambda''S \rangle|^2 \\ &= |\langle n'v' | \langle n'\lambda'S | \mu_{\lambda'\lambda''} | n''\lambda''S \rangle | n''v'' \rangle|^2. \end{aligned}$$

Neglecting the dependence of the electronic part of the matrix element on the internuclear distance (Franck-Condon approximation), we then finally obtain

$$\begin{aligned} & |\langle n'v'\lambda'S | \mu_{\lambda'\lambda''} | n''v''\lambda''S \rangle|^2 \\ &= |\langle n'v' | n''v'' \rangle|^2 |\langle n'\lambda'S | \mu_{\lambda'\lambda''} | n''\lambda''S \rangle|^2 \quad (52) \\ &= q_{v'v''} |\langle n'\lambda'S | \mu_{\lambda'\lambda''} | n''\lambda''S \rangle|^2, \end{aligned}$$

where we have introduced the well-known Franck-Condon factor $q_{v'v''} = |\langle n'v' | n''v'' \rangle|^2$.

10. SUM RULES

The Hönl-London factors of eq. (51) are known to obey a simple and general sum rule (Whiting and Nicholls (7)). To derive this sum rule we start by a summation over all the substates k' and k'' for fixed J' and J'' :

$$\mathcal{F}_{J'J''} = \sum_{k', k''} \mathcal{F}_{k'J'k''J''} .$$

The final sum rule then follows by summation of $\mathcal{F}_{J'J''}$ over J' or J'' .

However, we have to be very cautious in the derivation of the sum rules due to the special cases discussed in connection with eq. (37), and which obviously also apply to eq. (49).

We shall first consider the general and most simple case of $\Lambda' \neq 0$ and $\Lambda'' \neq 0$. In this case we notice that $\Lambda' + \Lambda'' > 1$, and there is accordingly no parity-dependent contribution in eq. (49). From eqs. (51) and (49) and the unitarity of the U-matrix we easily obtain

$$\mathcal{F}_{J'J''}^2 = (2J'+1)(2J''+1) \sum_{\Sigma} \begin{pmatrix} J' & 1 & J'' \\ \Lambda'+\Sigma & -(\Lambda'-\Lambda'') & -\Lambda''-\Sigma \end{pmatrix}^2 . \quad (53)$$

In the next step we calculate

$$\mathcal{F}_{J'} = \sum_{J''} \mathcal{F}_{J'J''} = (2J'+1) \sum_{\Sigma} \sum_{J''} (2J''+1) \begin{pmatrix} J' & 1 & J'' \\ \Lambda'+\Sigma & -(\Lambda'-\Lambda'') & -\Lambda''-\Sigma \end{pmatrix}^2 .$$

The summation over J'' in the expression above is easily worked out by use of the orthogonality relations of the $3j$ -symbols (cf. appendix) and the result is simply the number 1. Hence, we have

$$\mathcal{F}_{J'} = (2J'+1) \sum_{\Sigma} 1 = (2S+1)(2J'+1) .$$

In a similar way we would obtain

$$\mathcal{F}_{J''} = \sum_{J'} \mathcal{F}_{J'J''} = (2S+1)(2J''+1) .$$

The results obtained are parity-independent, and summing over the two parities and noting the symmetry in J' and J'' , we have the final sum rule for a transition with $\Lambda' \neq 0$ and $\Lambda'' \neq 0$:

$$g_J = 2(2S+1)(2J+1). \quad (54)$$

Next we have to consider several special cases:

- 1) $\Lambda' \neq 0, \Lambda'' = 0, S = \text{half-integral}$
- 2) $\Lambda' \neq 0, \Lambda'' = 0, S = \text{integral}$
- 3) $\Lambda' = \Lambda'' = 0, S = \text{half-integral}$
- 4) $\Lambda' = \Lambda'' = 0, S = \text{integral}.$

Sum rules were derived by calculations similar to those leading to eq. (54) for all the cases 1) - 4) above. For cases 1) and 2) the results were identical to eq. (54), whereas for cases 3) and 4) we obtained

$$g_J = (2S+1)(2J+1).$$

Finally, we then have the following general sum rule covering all cases (Whiting and Nicholls (7)): Summation of the Hönl-London factors of all the transitions originating from all the sublevels of a given rotational quantum number J yields

$$g_J = (2 - \delta_{0, \Lambda'+\Lambda''}) (2S+1)(2J+1). \quad (55)$$

The general sum rule of eq. (55) will not apply to singular levels for which the whole multiplicity of the electronic state is not fully developed. The singular levels are defined by

$$J < \Lambda + \sum_{\max} = \Lambda + S.$$

The reason is seen from eq. (53). For singular levels ($J < \Lambda + S$) the $3j$ -symbols are zero for one or more E -values. Hence, the summation over E in eq. (53) is disturbed, and the multiplicity factor $2S + 1$ does not result.

In numerical computations of the Hönl-London factors the sum rule of eq. (55) is of great help, as it yields a check of the computed results. Eq. (55) will be exactly fulfilled if exact numerical values are used for the expansion coefficients of eq.

(48). Deviations from eq. (55) will, however, certainly occur if analytic approximations to the expansion coefficients are made in such a way that the unitarity of the U-matrix is broken.

11. CONCLUDING REMARKS

In the present paper it has been the aim to give a consistent and simplified discussion of the theory of the intensities of rotational lines in diatomic spectra. The presentation is believed to be consistent since a common and simple mathematical formalism has been used throughout the paper. Furthermore, all mathematical formulae are derived from basic quantum mechanics, supposing only a rather elementary knowledge of the theory of diatomic spectra.

The presentation is based on spherical components of the transition operator, and the knowledge of a few elementary properties of the rotation matrices, which are the central concepts in the theory of the rotation group. No familiarity with group theory is, however, expected from the reader. The use of spherical components of the transition operator and the rotation matrices is particularly convenient for the transformations between space-fixed and molecule-fixed coordinate systems. In this way simple and symmetric expressions are obtained, which are easily handled by standard angular momentum theory. The traditional use of direction cosines for transforming between fixed- and rotating coordinate systems leads to rather intractable expressions, and should accordingly be avoided.

A main idea behind the present work has actually been to demonstrate how the symmetry properties of the rotational states

and the selection rules of the rotational spectra follow from simple properties of the rotation matrices, and from standard rules of angular momentum theory.

The theory of the intensities of diatomic spectral lines is certainly well established already, and no essential new results have been obtained. The theoretical results are, however, scattered through a considerable number of papers, based on different notations and different definitions of central concepts. Hence, there was an irresistible temptation to collect most of the important results in one study, and above all to demonstrate the power and elegance of the theory of the rotational symmetry in this connection. Anyway, new proofs of known relations have been produced, in particular for the general sum rule of eq. (55), the derivation of which seems rather cumbersome without use of the orthogonality relations of the $3j$ -symbols of angular momentum theory.

Finally, another motivation for the present work has been to advocate the use of a fully numeric approach for computing the Hönl-London factors or relative intensities. Eigenvalues and transition frequencies are now routinely computed by numerical diagonalization of the Hamiltonian matrix (cf. eq. (47)). This process also yields the expansion coefficients (eigenvectors, cf. eq. (48)) needed for an exact numerical computation of the Hönl-London factors. The analytic expressions which still seem to be in quite widespread use, are in most cases approximations, and since they are often also quite complex, they should now mainly be considered to belong to the pre-computer era.

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APPENDIX

The rotational operator $P(\alpha, \beta, \gamma)$ is defined to rotate a function through the general Eulerian angles α, β, γ with respect to a fixed coordinate system (X, Y, Z) as indicated in fig. 2 (10). The action of $P(\alpha, \beta, \gamma)$ on an angular momentum eigenfunction Ψ_{JM} is described by the rotation matrices, i.e.

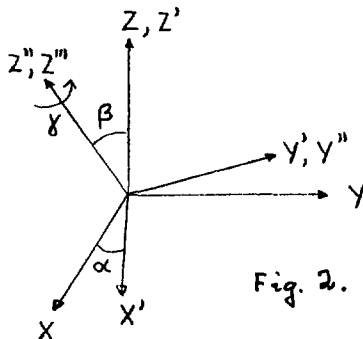


Fig. 2.

$$P(\alpha, \beta, \gamma) \Psi_{JM} = \sum_{M'} D_{M'M}^{(J)}(\alpha, \beta, \gamma) \Psi_{JM'} \quad (a1)$$

Whereas the rotation matrices depend on the angles α and γ in a simple way, there is a complex dependence on β , and a general element take the form

$$D_{M'M}^{(J)}(\alpha, \beta, \gamma) = e^{-iM'\alpha} d_{M'M}^{(J)}(\beta) e^{-iM\gamma} \quad (a2)$$

The β -dependence may be looked up in standard texts (9,10), and is not reproduced here.

A few basic properties of the rotation matrices are listed below:

$$D_{M'M}^{(J)}(\alpha, \beta, \gamma)^* = (-1)^{M'-M} D_{-M'-M}^{(J)}(\alpha, \beta, \gamma) \quad (a3)$$

$$d_{M'M}^{(J)}(\beta) = d_{-M-M'}^{(J)}(\beta)$$

$$d_{M'M}^{(J)}(\pi-\beta) = (-1)^{J-M'} d_{M-M'}^{(J)}(\beta) \quad (a4)$$

The product of two elements of two different rotation matrices will be needed, and is given by:

$$D_{M'_1 M_1}^{(J_1)}(\alpha, \beta, \gamma) D_{M'_2 M_2}^{(J_2)}(\alpha, \beta, \gamma) \quad (a5)$$

$$= \sum_J \sum_{M, M'} (2J+1) \begin{pmatrix} J_1 & J_2 & J \\ M'_1 & M'_2 & M \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} D_{M' M}^{(J)}(\alpha, \beta, \gamma)^*$$

Finally, we will also need to know the integral over a product of three rotation matrix elements:

$$\int_0^{2\pi} \int_0^{2\pi} \int_0^\pi D_{M'_1 M_1}^{(J_1)}(\alpha, \beta, \gamma) D_{M'_2 M_2}^{(J_2)}(\alpha, \beta, \gamma) D_{M'_3 M_3}^{(J_3)}(\alpha, \beta, \gamma) \sin\beta d\beta d\alpha d\gamma$$

$$= 8\pi^2 \begin{pmatrix} J_1 & J_2 & J_3 \\ M'_1 & M'_2 & M'_3 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}. \quad (a6)$$

In eqs. (a5) and (a6) we have introduced the 3j-symbols which will be defined below.

We also note that eq. (a1) applies to the components of a so called spherical tensor (10), in particular to the spherical components of a vector (cf. eq. (6)), and we have ($J = 1$ for a vector, i.e. tensor of rank 1):

$$\mu'_m = D(\alpha, \beta, \gamma) \mu_m = \sum_{m'} D_{m' m}^{(1)}(\alpha, \beta, \gamma) \mu_{m'}, \quad (a7)$$

where μ'_m now denotes a spherical component of $\underline{\mu}$ in the rotated (molecule-fixed) coordinate system, expressed in terms of the space-fixed components μ_m . Inverting eq. (a7) we get a space-fixed component in terms of the molecule-fixed ones (cf. eq. (38)),

$$\mu_m = \sum_{m'} D_{m m'}^{(1)}(\alpha, \beta, \gamma)^* \mu'_{m'}. \quad (a8)$$

The $3j$ -symbols introduced in eqs. (a5) and (a6) are related to the Clebsch-Gordan coefficients of angular momentum coupling theory:

$$\begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} = (-1)^{J_1 - J_2 - M} (2J+1)^{-1/2} \langle J_1, J_2, M_1, M_2 | J, J_2, J-M \rangle. \quad (a9)$$

Several simple symmetry rules apply to the $3j$ -symbols (10). In the present context it is of particular importance to recall that

$$\begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} = 0$$

for $J < |J_1 - J_2|$ or $J > J_1 + J_2$, or for $M_1 + M_2 + M \neq 0$. The two following orthogonality relations for the $3j$ -symbols have been used in the present work (10):

$$\sum_{M_1, M_2} (2J+1) \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J' \\ M_1 & M_2 & M' \end{pmatrix} = \delta_{JJ'} \delta_{MM'} \quad (a10)$$

$$\sum_{J, M} (2J+1) \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J \\ M'_1 & M'_2 & M \end{pmatrix} = \delta_{M_1 M'_1} \delta_{M_2 M'_2}.$$

Algebraic expressions for the general $3j$ -symbol are given by Brink and Satchler (10), who also give tabulations for several special cases.