Energy Levels and Line Intensities of Diatomic Molecules. Application to Alkali Metal Molecules#

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Calculation of rotational level energies and line intensities of diatomic molecules and its application to alkali metal diatomic molecules are reported. The effects of spin–orbit interaction, rotational interaction, spin–rotation interaction, spin–spin interaction, hyperfine interaction, and Zeeman interaction are considered.

The advent of a tunable narrow line laser opened a new world of high resolution spectroscopy.[1,2] In addition to level energies, line intensities and line shapes became useful to study the molecular structure and the dynamics. Alkali metal diatomic molecules have the absorption bands of electronic transitions in the visible region, and have been used to invent new methods of laser spectroscopy. An appropriate molecule can be chosen from a series of alkali metal molecules depending on the scientific interest. Alkali metal molecules are very useful to study the dissociation dynamics because the dissociated atoms have the radiative transition (such as the D_1 and D_2 lines) in visible. The quantum mechanical calculation of the energy levels and line intensities is essential to study the molecular spectra. Very good books[3—8] on this subject have been published, but it is now important to get the formulae which include the orientational quantum number. The calculation and its application to alkali metal diatomic molecules are reported in this article.

1. Rotational Energy Levels

(A) Hamiltonian. The Hamiltonian for a rotating diatomic molecule in the absence of an external field can be written in the form

$$H = H_e + H_v + H_r, \tag{1}$$

where H_e is the electronic part, and H_v is the vibrational part. The rotational part H_r is written as[5]

$$\begin{aligned} H_r &= B[(J_x - L_x - S_x)^2 + (J_y - L_y - S_y)^2] \\ &= B[(\boldsymbol{J}^2 - J_z{}^2) + (\boldsymbol{L}^2 - L_z^2) + (\boldsymbol{S}^2 - S_z^2) \\ &\quad +(L_+S_- + L_-S_+) - (J_+L_- + J_-L_+) \\ &\quad -(J_+S_- + J_-S_+)], \end{aligned} \tag{2}$$

where $B=\hbar^2/2\mu R^2$, μ is a reduced mass, and R is an internuclear distance. The rotational angular momentum is expressed as the total angular momentum ($\boldsymbol{J}$) minus the electronic orbital and spin angular momenta ($\boldsymbol{L}$ and $\boldsymbol{S}$). $J_\pm = J_x \pm iJ_y$, $L_\pm = L_x \pm iL_y$, $S_\pm = S_x \pm iS_y$, and the suffixes x and y denote the components of the molecule-fixed coordinates, and the z axis is along its internuclear axis. In a diatomic molecule, only the z-component of the electronic orbital angular momentum is a constant of the motion because of the electrostatic interaction between the electrons and the axial field.

(B) Basic Functions. As a set of basis functions, we use wave functions of simple products, $|\Lambda>|S\Sigma>|v>|J\Omega M>$. The function $|\Lambda>|S\Sigma>|v>$ is a wave function for a nonrotating molecule, where Λ and Σ represent the projections of the total electronic orbital and total electronic spin angular momenta along the molecular axis, respectively, and v represents the vibrational quantum number. All of these are expressed in molecule-fixed coordinates. The wave function $|J\Omega M>$ of the rotational part is expressed as[9]

$$|J\Omega M> = (-)^{M-\Omega}[(2J+1)/(8\pi^2)]^{1/2} D^J_{-M-\Omega}, \tag{3}$$

where the quantum numbers J and M specify the total angular momentum and its projection along the laboratory-fixed Z axis, respectively, and $\Omega=\Lambda+\Sigma$. We shall always use the representation of the rotation group, the angular momenta, the coupling coefficients and tensors defined by Brink and Satchler.[9]

(C) Matrix Elements of Angular Momenta. The nonvanishing matrix elements of the components of the spin angular momentum operator $\boldsymbol{S}$ and the orbital angular momentum operator $\boldsymbol{L}$ are the following:

$$\begin{aligned} &< S\Sigma|\boldsymbol{S}^2|S\Sigma> = S(S+1), \\ &< S\Sigma|S_z|S\Sigma> = \Sigma, \\ &< S\Sigma \pm 1|S_\pm|S\Sigma> = [(S \mp \Sigma)(S \pm \Sigma + 1)]^{1/2} \\ &\qquad\qquad = [S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}, \\ &< L\Lambda|\boldsymbol{L}^2|L\Lambda> = L(L+1), \\ &< L\Lambda|L_z|L\Lambda> = \Lambda, \\ &< L\Lambda \pm 1|L_\pm|L\Lambda> = [(L \mp \Lambda)(L \pm \Lambda + 1)]^{1/2} \\ &\qquad\qquad = [L(L+1) - \Lambda(\Lambda \pm 1)]^{1/2}. \end{aligned} \tag{4}$$

When electrons are in Rydberg orbitals, L is a good quantum number. In general, electrostatic interactions between the electrons and the axial field of a diatomic molecule are large. Hence, electronic wave functions are not eigenfunctions of $\boldsymbol{L}^2$, and L is not a good quantum number. Λ is a good quantum number of L_z, and the

#This paper is dedicated to the late Professor Hiroshi Kato.

wave function of the electronic orbital part is expressed as $|\Lambda>$. The nonvanishing matrix elements of the total angular momentum $\boldsymbol{J}$ are similar, but the matrix elements of $J_\pm$ are different. We must be careful on this somewhat surprising difference in behavior of $\boldsymbol{J}$ from $\boldsymbol{L}$ and $\boldsymbol{S}$.[5,10]

$$\begin{aligned}
&< J\Omega|\boldsymbol{J}^2|J\Omega >= J(J+1),\\
&< J\Omega|J_z|J\Omega >= \Omega,\\
&< J\Omega \mp 1|J_\pm|J\Omega >= [(J \pm \Omega)(J \mp \Omega + 1)]^{1/2}\\
&\qquad = [J(J+1) - \Omega(\Omega \mp 1)]^{1/2}. \quad (5)
\end{aligned}$$

$|J\Omega M>$ defined by Eq. 3 satisfies the relation of Eq. 5.

(D) Spin-Orbit Interaction. The operator of the spin–orbit interaction is represented by $A\boldsymbol{L}\cdot\boldsymbol{S}$ or $\sum_i \xi(r_i)\boldsymbol{l}_i\cdot\boldsymbol{s}_i$, where $\boldsymbol{l}_i$ and $\boldsymbol{s}_i$ are operators representing the electronic orbital and electronic spin angular momenta of the i-th electron. The operator

$$H_{so} = A\boldsymbol{L}\cdot\boldsymbol{S} \quad (6)$$

is used to compute spin–orbit splittings within a given spin multiplet. The operator

$$H_{so} = \sum_i \xi(r_i)\boldsymbol{l}_i\cdot\boldsymbol{s}_i \quad (7)$$

must be used to compute the interaction between states belonging to different S or L values. Matrix elements of $A\boldsymbol{L}\cdot\boldsymbol{S}$ are[5]

$$\begin{aligned}
&< S\Sigma| < \Lambda|A\boldsymbol{L}\cdot\boldsymbol{S}|\Lambda > |S\Sigma >= A\Lambda\Sigma,\\
&< S\Sigma| < \Lambda|A\boldsymbol{L}\cdot\boldsymbol{S}|\Lambda' > |S'\Sigma' >= 0\\
&\qquad \text{if } |\Lambda > |S\Sigma > \neq |\Lambda' > |S'\Sigma' > . \quad (8)
\end{aligned}$$

(E) Molecular States Obtainable from the Union of Two Atoms. Possible electronic configurations resulting from the union of two atoms in specified states can be obtained by applying the general rules.[11]

If the molecules can be described in terms of Hund's coupling cases (a) and (b), the electronic states derived from specified atomic states of the same element are

[A]: $^1\Sigma_g^+$, $^3\Sigma_u^+$ for $^2S + {}^2S$,
[B]: $^1\Pi_g$, $^3\Pi_g$, $^1\Pi_u$, $^3\Pi_u$, $^1\Sigma_g^+$, $^3\Sigma_g^+$, $^1\Sigma_u^+$, $^3\Sigma_u^+$ for $^2P + {}^2S$,
[C]: $^1\Pi_g$, $^3\Pi_g$, $^1\Pi_u$, $^3\Pi_u$, $^1\Sigma_g^+$, $^3\Sigma_g^+$, $^1\Sigma_u^+$, $^3\Sigma_u^+$, $^1\Delta_g$, $^3\Delta_g$, $^1\Delta_u$, $^3\Delta_u$ for $^2D + {}^2S$,

and those of different elements are

[A′]: $^1\Sigma^+$, $^3\Sigma^+$ for $^2S + {}^2S$,
[B′]: $^1\Pi$, $^3\Pi$, $^1\Sigma^+$, $^3\Sigma^+$ for $^2P + {}^2S$,
[C′]: $^1\Pi$, $^3\Pi$, $^1\Sigma^+$, $^3\Sigma^+$, $^1\Delta$, $^3\Delta$ for $^2D + {}^2S$.

Simple molecular orbitals for homonuclear diatomic molecules formed from pairs of atomic orbitals are

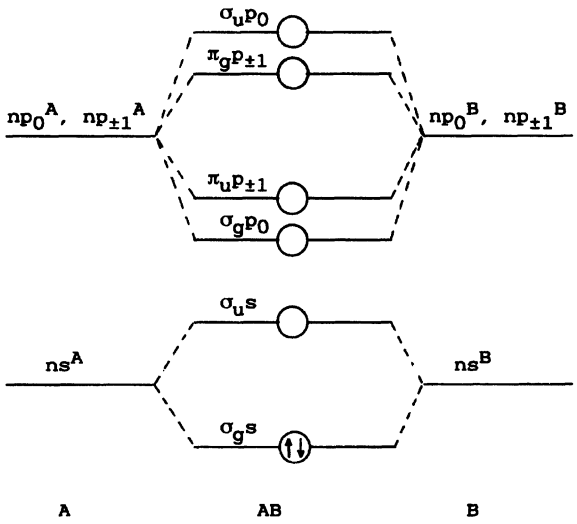


Fig. 1. Energy diagram for molecular orbitals of a homonuclear diatomic molecule and the electron configuration in the ground state of alkali metal molecules. *ns–np* mixing is neglected.

$$\begin{aligned}
&\sigma_u s = 2^{-1/2}(ns^A - ns^B),\ \sigma_g s = 2^{-1/2}(ns^A + ns^B),\\
&\pi_g p_{\pm1} = 2^{-1/2}(np^A_{\pm1} - np^B_{\pm1}),\\
&\pi_u p_{\pm1} = 2^{-1/2}(np^A_{\pm1} + np^B_{\pm1}),\\
&\sigma_u p_0 = 2^{-1/2}(np^A_0 + np^B_0),\ \sigma_g p_0 = 2^{-1/2}(np^A_0 - np^B_0),
\end{aligned}$$

where $np^N_0 = np^N_z$, and $np^N_{\pm1} = \mp 2^{-1/2}(np^N_x \pm i np^N_y)$ for N=A and B. The overlap integral is neglected for the normalization. The energy diagram for the molecular orbitals and the electronic configuration for the ground state of alkali metal diatomic molecules are schematically shown in Fig. 1.

In the case of an alkali metal diatomic molecule of the same element, the electronic wave functions for group [A] are approximately expressed in terms of simple molecular orbitals as

$$\begin{aligned}
|X^1\Sigma_g^+ > &= |(\sigma_g s)(\overline{\sigma_g s})| = |0^+ > |0\ 0 >,\\
|a^3\Sigma_u^+ > &: |(\sigma_g s)(\sigma_u s)| = |0^+ > |1\ 1 >,\\
&\quad |(\overline{\sigma_g s})(\overline{\sigma_u s})| = |0^+ > |1\ -1 >,\\
\text{and } &(2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_u s})| + |(\overline{\sigma_g s})(\sigma_u s)|]\\
&= |0^+ > |1\ 0 >, \quad (9)
\end{aligned}$$

where factors of normalization for the determinant functions are omitted, orbital $(\cdots)$ denotes a molecular orbital with spin α, orbital $(\overline{\cdots})$ denotes an orbital with spin β, and the last symbols denote $|\Lambda>|S\Sigma>$.

The electronic wave functions for group [B] are

$$\begin{aligned}
|A^1\Sigma_u^+ > &= (2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_u p_0})| - |(\overline{\sigma_g s})(\sigma_u p_0)|]\\
&= |0^+ > |0\ 0 >,\\
|B^1\Pi_u > &= (2)^{-1/2}[|(\sigma_g s)(\overline{\pi_u p_{\pm1}})| - |(\overline{\sigma_g s})(\pi_u p_{\pm1})|]\\
&= |\pm 1 > |0\ 0 >,\\
|b^3\Pi_u > &: |(\sigma_g s)(\pi_u p_{\pm1})| = |\pm 1 > |1\ 1 >,
\end{aligned}$$

$$
\begin{aligned}
&|(\overline{\sigma_g s})(\overline{\pi_u p_{\pm1}})| = |\pm1>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\pi_u p_{\pm1}})| + |(\overline{\sigma_g s})(\pi_u p_{\pm1})|]\\
&\qquad = |\pm1>|1\,0>,\\
&|(2)^1\Sigma_g^+> = (2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_g p_0})| - |(\overline{\sigma_g s})(\sigma_g p_0)|]\\
&\qquad = |0^+>|0\,0>,\\
&|(1)^3\Sigma_g^+> : |(\sigma_g s)(\sigma_g p_0)| = |0^+>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\sigma_g p_0})| = |0^+>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_g p_0})| + |(\overline{\sigma_g s})(\sigma_g p_0)|]\\
&\qquad = |0^+>|1\,0>,\\
&|(1)^1\Pi_g> = (2)^{-1/2}[|(\sigma_g s)(\overline{\pi_g p_{\pm1}})| - |(\overline{\sigma_g s})(\pi_g p_{\pm1})|]\\
&\qquad = |\pm1>|0\,0>,\\
&|(1)^3\Pi_g> : |(\sigma_g s)(\pi_g p_{\pm1})| = |\pm1>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\pi_g p_{\pm1}})| = |\pm1>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\pi_g p_{\pm1}})| + |(\overline{\sigma_g s})(\pi_g p_{\pm1})|]\\
&\qquad = |\pm1>|1\,0>,\\
&|c^3\Sigma_u^+> : |(\sigma_g s)(\sigma_u p_0)| = |0^+>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\sigma_u p_0})| = |0^+>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_u p_0})| + |(\overline{\sigma_g s})(\sigma_u p_0)|]\\
&\qquad = |0^+>|1\,0>. \qquad (10)
\end{aligned}
$$

The electronic wave functions for group [C] are

$$
\begin{aligned}
&|D^1\Sigma_u^+> = (2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_u d_0})| - |(\overline{\sigma_g s})(\sigma_u d_0)|]\\
&\qquad = |0^+>|0\,0>,\\
&|e^3\Sigma_u^+> : |(\sigma_g s)(\sigma_u d_0)| = |0^+>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\sigma_u d_0})| = |0^+>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_u d_0})| + |(\overline{\sigma_g s})(\sigma_u d_0)|]\\
&\qquad = |0^+>|1\,0>,\\
&|C^1\Pi_u> = (2)^{-1/2}[|(\sigma_g s)(\overline{\pi_u d_{\pm1}})| - |(\overline{\sigma_g s})(\pi_u d_{\pm1})|]\\
&\qquad = |\pm1>|0\,0>,\\
&|d^3\Pi_u> : |(\sigma_g s)(\pi_u d_{\pm1})| = |\pm1>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\pi_u d_{\pm1}})| = |\pm1>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\pi_u d_{\pm1}})| + |(\overline{\sigma_g s})(\pi_u d_{\pm1})|]\\
&\qquad = |\pm1>|1\,0>,\\
&|^1\Delta_u> = (2)^{-1/2}[|(\sigma_g s)(\overline{\delta_u d_{\pm2}})| - |(\overline{\sigma_g s})(\delta_u d_{\pm2})|]\\
&\qquad = |\pm2>|0\,0>,\\
&|^3\Delta_u> : |(\sigma_g s)(\delta_u d_{\pm2})| = |\pm2>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\delta_u d_{\pm2}})| = |\pm2>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\delta_u d_{\pm2}})| + |(\overline{\sigma_g s})(\delta_u d_{\pm2})|]\\
&\qquad = |\pm2>|1\,0>,\\
&|(3)^1\Sigma_g^+> = (2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_g d_0})| - |(\overline{\sigma_g s})(\sigma_g d_0)|]\\
&\qquad = |0^+>|0\,0>,\\
&|(2)^3\Sigma_g^+> : |(\sigma_g s)(\sigma_g d_0)| = |0^+>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\sigma_g d_0})| = |0^+>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\sigma_g d_0})| + |(\overline{\sigma_g s})(\sigma_g d_0)|]\\
&\qquad = |0^+>|1\,0>,\\
&|(2)^1\Pi_g> = (2)^{-1/2}[|(\sigma_g s)(\overline{\pi_g d_{\pm1}})| - |(\overline{\sigma_g s})(\pi_g d_{\pm1})|]\\
&\qquad = |\pm1>|0\,0>,\\
&|(2)^3\Pi_g> : |(\sigma_g s)(\pi_g d_{\pm1})| = |\pm1>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\pi_g d_{\pm1}})| = |\pm1>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\pi_g d_{\pm1}})| + |(\overline{\sigma_g s})(\pi_g d_{\pm1})|]\\
&\qquad = |\pm1>|1\,0>,\\
&|^1\Delta_g> = (2)^{-1/2}[|(\sigma_g s)(\overline{\delta_g d_{\pm2}})| - |(\overline{\sigma_g s})(\delta_g d_{\pm2})|]\\
&\qquad = |\pm2>|0\,0>,\\
&|^3\Delta_g> : |(\sigma_g s)(\delta_g d_{\pm2})| = |\pm2>|1\,1>,\\
&\qquad |(\overline{\sigma_g s})(\overline{\delta_g d_{\pm2}})| = |\pm2>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma_g s)(\overline{\delta_g d_{\pm2}})| + |(\overline{\sigma_g s})(\delta_g d_{\pm2})|]\\
&\qquad = |\pm2>|1\,0>. \qquad (11)
\end{aligned}
$$

In the case of an alkali metal diatomic molecule of different elements, the electronic wave functions for group [A′] are approximately expressed in terms of simple molecular orbitals.

$$
\begin{aligned}
&|^1\Sigma^+> = |(\sigma s)(\overline{\sigma s})| = |0^+>|0\,0>,\\
&|^3\Sigma^+> : |(\sigma s)(\sigma s^*)| = |0^+>|1\,1>,\\
&\qquad |(\overline{\sigma s})(\overline{\sigma s^*})| = |0^+>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma s)(\overline{\sigma s^*})| + |(\overline{\sigma s})(\sigma s^*)|] = |0^+>|1\,0>. \qquad (12)
\end{aligned}
$$

The electronic wave functions for group [B′] are:

$$
\begin{aligned}
&|^1\Sigma^+> = (2)^{-1/2}[|(\sigma s)(\overline{\sigma p_0})| - |(\overline{\sigma s})(\sigma p_0)|]\\
&\qquad = |0^+>|0\,0>,\\
&|^3\Sigma^+> : |(\sigma s)(\sigma p_0)| = |0^+>|1\,1>,\\
&\qquad |(\overline{\sigma s})(\overline{\sigma p_0})| = |0^+>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma s)(\overline{\sigma p_0})| + |(\overline{\sigma s})(\sigma p_0)|]\\
&\qquad = |0^+>|1\,0>,\\
&|^1\Pi> = (2)^{-1/2}[|(\sigma s)(\overline{\pi p_{\pm1}})| - |(\overline{\sigma s})(\pi p_{\pm1})|]\\
&\qquad = |\pm1>|0\,0>,\\
&|^3\Pi> : |(\sigma s)(\pi p_{\pm1})| = |\pm1>|1\,1>,\\
&\qquad |(\overline{\sigma s})(\overline{\pi p_{\pm1}})| = |\pm1>|1-1>,\\
&\text{and } (2)^{-1/2}[|(\sigma s)(\overline{\pi p_{\pm1}})| + |(\overline{\sigma s})(\pi p_{\pm1})|]\\
&\qquad = |\pm1>|1\,0>. \qquad (13)
\end{aligned}
$$

(F) Eigenfunction and Eigenvalue. The eigenfunction and eigenvalue can be obtained by solving the secular equation composed of the matrices for $H = H_e + H_v + H_r + H_{so}$ in terms of the basis set $|\Lambda> |S\Sigma> |v> |J\Omega M>$.

i) $^1\Sigma^+$ State. Matrix element for a $^1\Sigma^+$ state, whose basis set function is $|0^+>|00>|v>|J0M>$, is given by

$$
\begin{aligned}
&< J0M| < v| < 00| < 0^+|H|0^+> |00> |v> |J0M>\\
&\qquad = E + B_v[J(J+1) + < L_\perp^2 >], \qquad (14)
\end{aligned}
$$

where E represents the vibrational-electronic energy, $B_v = < v|B|v >$, and $< L_\perp^2 >$ is the matrix elements of $(\boldsymbol{L}^2 - L_z^2)$. The eigenfunction for a level of the state $^1\Sigma^+$ is

$$|^1\Sigma^+ vJM>=|0^+>|00>|v>|J0M>. \quad (15)$$

The eigenvalue is

$$E(^1\Sigma^+ vJM)=E+B_v[J(J+1)+<L_\perp^2>]. \quad (16)$$

ii) $^1\Pi$ State. Matrix elements for a $^1\Pi$ state, whose basis set functions are $|1>|00>|v>|J1M>$ and $|-1>|00>|v>|J-1M>$, are given by

$$\begin{aligned}
&<J1M|<v|<00|<1|H|1>|00>|v>|J1M> \\
&\quad =E+B_v[J(J+1)-1+<L_\perp^2>], \\
&<J1M|<v|<00|<1|H|-1>|00>|v>|J-1M> \\
&\quad =0, \\
&<J-1M|<v|<00|<-1|H|-1>|00>|v>|J-1M> \\
&\quad =E+B_v[J(J+1)-1+<L_\perp^2>]. \quad (17)
\end{aligned}$$

The eigenfunctions with a well-defined parity for levels of the state $^1\Pi$ are

$$\begin{aligned}
|^1\Pi\pm vJM>=2^{-1/2}(&|1>|00>|v>|J1M> \\
&\pm|-1>|00>|v>|J-1M>). \quad (18)
\end{aligned}$$

The eigenvalues are

$$E(^1\Pi\pm vJM)=E+B_v[J(J+1)-1+<L_\perp^2>]. \quad (19)$$

iii) $^3\Sigma^+$ State. The symmetric matrix elements for a $^3\Sigma^+$ state, whose basis set functions are $|0^+>|11>|v>|J1M>$, $|0^+>|10>|v>|J0M>$, and $|0^+>|1-1>|v>|J-1M>$, are given by

$$\begin{aligned}
&<J1M|<v|<11|<0^+|H|0^+>|11>|v>|J1M> \\
&\quad =E+B_v[J(J+1)+<L_\perp^2>], \\
&<J1M|<v|<11|<0^+|H|0^+>|10>|v>|J0M> \\
&\quad =-B_v[2J(J+1)]^{1/2}, \\
&<J1M|<v|<11|<0^+|H|0^+>|1-1> \\
&\quad |v>|J-1M>=0, \\
&<J0M|<v|<10|<0^+|H|0^+>|10>|v>|J0M> \\
&\quad =E+B_v[J(J+1)+2+<L_\perp^2>], \\
&<J0M|<v|<10|<0^+|H|0^+>|1-1> \\
&\quad |v>|J-1M>=-B_v[2J(J+1)]^{1/2}, \\
&<J-1M|<v|<1-1|<0^+|H|0^+>|1-1> \\
&\quad |v>|J-1M>=E+B_v[J(J+1)+<L_\perp^2>]. \quad (20)
\end{aligned}$$

The eigenfunctions for levels of the state $^3\Sigma^+$ are

$$\begin{aligned}
&|^3\Sigma^+ vN=J+1JM> \\
&\quad =[J/2(2J+1)]^{1/2}(|0^+>|11>|v>|J1M> \\
&\qquad +|0^+>|1-1>|v>|J-1M>) \\
&\qquad -[(J+1)/(2J+1)]^{1/2}|0^+>|10>|v>|J0M>, \\
&|^3\Sigma^+ vN=JJM> \\
&\quad =2^{-1/2}(|0^+>|11>|v>|J1M> \\
&\qquad -|0^+>|1-1>|v>|J-1M>), \\
&|^3\Sigma^+ vN=J-1JM> \\
&\quad =[(J+1)/2(2J+1)]^{1/2}(|0^+>|11>|v>|J1M> \\
&\qquad +|0^+>|1-1>|v>|J-1M>) \\
&\qquad +[J/(2J+1)]^{1/2}|0^+>|10>|v>|J0M>, \quad (21)
\end{aligned}$$

where N is the rotational quantum number. The eigenvalues are

$$E(^3\Sigma^+ vNJM)=E+B_v[N(N+1)+<L_\perp^2>]. \quad (22)$$

The symbols F_1, F_2, F_3 refer to states of $J=N+1$, $J=N$, $J=N-1$.

iv) $^3\Pi$ State. The nonvanishing symmetric matrix elements for a $^3\Pi$ state, whose basis set functions are $|1>|1-1>|v>|J0M>$, $|1>|10>|v>|J1M>$, $|1>|11>|v>|J2M>$, $|-1>|11>|v>|J0M>$, $|-1>|10>|v>|J-1M>$, and $|-1>|1-1>|v>|J-2M>$, are given by

$$\begin{aligned}
&<J0M|<v|<1-1|<1|H|1>|1-1>|v>|J0M> \\
&\quad =E-A+B_v[J(J+1)+1+<L_\perp^2>], \\
&<J0M|<v|<1-1|<1|H|1>|10>|v>|J1M> \\
&\quad =-B_v[2J(J+1)]^{1/2}, \\
&<J1M|<v|<10|<1|H|1>|10>|v>|J1M> \\
&\quad =E+B_v[J(J+1)+1+<L_\perp^2>], \\
&<J1M|<v|<10|<1|H|1>|11>|v>|J2M> \\
&\quad =-B_v[2(J+2)(J-1)]^{1/2}, \\
&<J2M|<v|<11|<1|H|1>|11>|v>|J2M> \\
&\quad =E+A+B_v[J(J+1)-3+<L_\perp^2>], \\
&<J0M|<v|<11|<-1|H|-1>|11>|v>|J0M> \\
&\quad =E-A+B_v[J(J+1)+1+<L_\perp^2>], \\
&<J0M|<v|<11|<-1|H|-1>|10>|v> \\
&\quad |J-1M>=-B_v[2J(J+1)]^{1/2}, \\
&<J-1M|<v|<10|<-1|H|-1>|10>|v> \\
&\quad |J-1M>=E+B_v[J(J+1)+1+<L_\perp^2>], \\
&<J-1M|<v|<10|<-1|H|-1>|1-1>|v> \\
&\quad |J-2M>=-B_v[2(J+2)(J-1)]^{1/2}, \\
&<J-2M|<v|<1-1|<-1|H|-1>|1-1>|v> \\
&\quad |J-2M>=E+A+B_v[J(J+1)-3+<L_\perp^2>], \quad (23)
\end{aligned}$$

where A is the spin-orbit coupling constant defined by Eq. 6.

In case of $A \gg B_v J$ (Hund's case (a)), the eigenfunctions for levels of the $^3\Pi$ state are

$$\begin{aligned}
&|^3\Pi_0\pm vJM>=2^{-1/2}(|1>|1-1>|v>|J0M> \\
&\qquad \pm|-1>|11>|v>|J0M>), \\
&|^3\Pi_1\pm vJM>=2^{-1/2}(|1>|10>|v>|J1M> \\
&\qquad \pm|-1>|10>|v>|J-1M>), \\
&|^3\Pi_2\pm vJM>=2^{-1/2}(|1>|11>|v>|J2M> \\
&\qquad \pm|-1>|1-1>|v>|J-2M>). \quad (24)
\end{aligned}$$

The eigenvalues are

$$E(^3\Pi_0 \pm vJM) = E - A + B_v[J(J+1) + 1 + < L_\perp^2 >],$$
$$E(^3\Pi_1 \pm vJM) = E + B_v[J(J+1) + 1 + < L_\perp^2 >],$$
$$E(^3\Pi_2 \pm vJM) = E + A + B_v[J(J+1) - 3 + < L_\perp^2 >]. \quad (25)$$

In case of $B_v J \gg A$ (Hund's case (b)), the eigenfunctions for levels of the $^3\Pi$ state are

$$|^3\Pi \pm vN = JJM > = (2)^{-1/2}|^3\Pi_0 \pm vJM > + [J(J+1)]^{-1/2}|^3\Pi_1 \pm vJM > - [(J-1)(J+2)/2J(J+1)]^{1/2}|^3\Pi_2 \pm vJM >,$$
$$|^3\Pi \pm vN = J-1JM > = [(J-1)/2(2J+1)]^{1/2}|^3\Pi_0 \pm vJM > + [(J-1)(J+1)/J(2J+1)]^{1/2}|^3\Pi_1 \pm vJM > + [(J+1)(J+2)/2J(2J+1)]^{1/2}|^3\Pi_2 \pm vJM >,$$
$$|^3\Pi \pm vN = J+1JM > = [(J+2)/2(2J+1)]^{1/2}|^3\Pi_0 \pm vJM > - [J(J+2)/(J+1)(2J+1)]^{1/2}|^3\Pi_1 \pm vJM > + [J(J-1)/2(J+1)(2J+1)]^{1/2}|^3\Pi_2 \pm vJM > . \quad (26)$$

The eigenvalues are

$$E(^3\Pi \pm vNJM) = E + B_v[N(N+1) - 1 + < L_\perp^2 >]. \quad (27)$$

(G) Symmetry Properties of the Rotational Energy Levels.[5,12]

i) Even (+) Parity and Odd (−) Parity. The rotational levels of all diatomic molecules are called to be of *even* (+) *parity* if the corresponding complete molecular wave functions are invariant to laboratory-fixed inversion operator I, and to be of *odd* (−) *parity* if the wave functions transform into their negative. The geometric symmetry operation $\sigma_v(xz)$ represents a reflection through the molecule-fixed xz plane. When $\sigma_v(xz)$ is applied to all (electronic, vibrational, and rotational) variables, it is equivalent to the laboratory-fixed inversion I. The effect of the operation σ_v on the basis set wave function is

$$\sigma_v|\Lambda > |S\Sigma > |v > |J\Omega M > = (-)^{s-\Lambda+S-\Sigma+J-\Omega} \times |-\Lambda > |S-\Sigma > |v > |J-\Omega M >, \quad (28)$$

where s=1 for Σ^- states, s=0 for all other states. Σ^+ and Σ^- are defined as $\sigma_v|\Sigma^+ > = +|\Sigma^+ >$, $\sigma_v|\Sigma^- > = -|\Sigma^- >$. For example, $|\Sigma^+ > = [\pi_{+1}(1)\pi_{-1}(2) + \pi_{-1}(1)\pi_{+1}(2)]/(2)^{1/2}$, and $|\Sigma^- > = [\pi_{+1}(1)\pi_{-1}(2) - \pi_{-1}(1)\pi_{+1}(2)]/(2)^{1/2}$.

The Hamiltonian $H = H_e + H_v + H_r$ is invariant under the symmetry operation σ_v. States of a definite parity transform into themselves or into their negative under this operation. Functions of the form

$$|\Lambda > |S\Sigma > |v > |J\Omega M > \pm |-\Lambda > |S-\Sigma > |v > |J-\Omega M > \quad (29)$$

have a definite parity as,

$$\sigma_v[|\Lambda > |S\Sigma > |v > |J\Omega M > + |-\Lambda > |S-\Sigma > |v > |J-\Omega M >] = (-)^{s-\Lambda+S-\Sigma+J-\Omega}[|\Lambda > |S\Sigma > |v > |J\Omega M > + |-\Lambda > |S-\Sigma > |v > |J-\Omega M >],$$
$$\sigma_v[|\Lambda > |S\Sigma > |v > |J\Omega M > - |-\Lambda > |S-\Sigma > |v > |J-\Omega M >] = -(-)^{s-\Lambda+S-\Sigma+J-\Omega}[|\Lambda > |S\Sigma > |v > |J\Omega M > - |-\Lambda > |S-\Sigma > |v > |J-\Omega M >].$$

For example,
$^1\Sigma^+$: $|0^+ > |00 > |v > |J0M >$ is parity even (+) for even J, parity odd (−) for odd J.

$^1\Pi$: $(|1 > |00 > |v > |J1M > + |-1 > |00 > |v > |J-1M >)/2^{1/2}$ is parity even (+) for even J, parity odd (−) for odd J. $(|1 > |00 > |v > |J1M > - |-1 > |00 > |v > |J-1M >)/2^{1/2}$ is parity odd (−) for even J, parity even (+) for odd J.

$^3\Sigma^+$: $|^3\Sigma^+ vN = JJM >$ is parity even (+) for even J, parity odd (−) for odd J. $|^3\Sigma^+ vN = J+1JM >$ and $|^3\Sigma^+ vN = J-1JM >$ are parity odd (−) for even J, parity even (+) for odd J.

$^3\Pi$: $(|1 > |1-1 > |v > |J0M > - |-1 > |11 > |v > |J0M >)/2^{1/2}$, $(|1 > |10 > |v > |J1M > - |-1 > |10 > |v > |J-1M >)/2^{1/2}$, $(|1 > |11 > |v > |J2M > - |-1 > |1-1 > |v > |J-2M >)/2^{1/2}$ are parity even (+) for even J, parity odd (−) for odd J. $(|1 > |1-1 > |v > |J0M > + |-1 > |11 > |v > |J0M >)/2^{1/2}$, $(|1 > |10 > |v > |J1M > + |-1 > |10 > |v > |J-1M >)/2^{1/2}$, $(|1 > |11 > |v > |J2M > + |-1 > |1-1 > |v > |J-2M >)/2^{1/2}$ are parity odd (−) for even J, parity even (+) for odd J.

ii) Labeling (*e*) and (*f*) of Parity Doublet Levels. For molecules with an even number of electrons (integral J), levels with parity $+(-)^J$ are called e levels, and levels with parity $-(-)^J$ are called f levels, where J is the quantum number for total angular momentum, omitting nuclear spin. For molecules with an odd number of electrons (half-integral J), levels with parity $+(-)^{J-0.5}$ are called e levels, and levels with parity $-(-)^{J-0.5}$ are called f levels. For example,
$^1\Sigma^+$: e level for all J.

$^1\Pi$: $(|1 > |00 > |v > |J1M > + |-1 > |00 > |v > |J-1M >)/2^{1/2}$ is e level for all J. $(|1 > |00 > |v > |J1M > - |-1 > |00 > |v > |J-1M >)/2^{1/2}$ is f level for all J.

$^3\Sigma^+$: $|^3\Sigma^+ vN = JJM >$ is e level for all J. $|^3\Sigma^+ vN = JJ+1M >$ and $|^3\Sigma^+ vN = JJ-1M >$ are f levels for all J.

$^3\Pi$: $(|1>|1-1>|v>|J0M>$
$-|-1>|11>|v>|J0M>)/2^{1/2}$,
$(|1>|10>|v>|J1M>$
$-|-1>|10>|v>|J-1M>)/2^{1/2}$, and
$(|1>|11>|v>|J2M>$
$-|-1>|1-1>|v>|J-2M>)/2^{1/2}$

are e levels for all J.

$(|1>|1-1>|v>|J0M>$
$+|-1>|11>|v>|J0M>)/2^{1/2}$,
$(|1>|10>|v>|J1M>$
$+|-1>|10>|v>|J-1M>)/2^{1/2}$, and
$(|1>|11>|v>|J2M>$
$+|-1>|1-1>|v>|J-2M>)/2^{1/2}$

are f levels for all J.

iii) Symmetric (s) and Antisymmetric (a). The rotational levels of homonuclear diatomic molecules are said to be *symmetric* (s) if the corresponding complete molecular wave functions are invariant to permutation P of identical nuclei. They are *antisymmetric* (a) if the wave functions transform into their negative.

The geometric symmetry operation $C_2(y)$, when it is applied to all variables, is equivalent to the permutation P of two identical nuclei, and

$$C_2(y) = \sigma_v(xz)i. \tag{30}$$

In a homonuclear diatomic molecule, the subscript u is indicated if the electronic orbital wave function changes the sign by the molecule-fixed inversion operation i, and the subscript g is indicated if it is invariant.

$$i|L\Lambda_g> = +|L\Lambda_g>,\ i|L\Lambda_u> = -|L\Lambda_u>,$$
$$i|S\Sigma> = +|S\Sigma>,\ i|J\Omega M> = +|J\Omega M>. \tag{31}$$

iv) Influence of Nuclear Spin. In a homonuclear diatomic molecule, the nuclear spin functions are symmetric for odd I and antisymmetric for even I, where I is the nuclear spin quantum number. Since the total wave function must be antisymmetric for nuclei of half-integral spin, the nuclear spin states of even I values are possible for the symmetric rotational levels and those of odd I values are possible for antisymmetric rotational levels.

		$^1\Sigma_g^+$		$^1\Sigma_u^+$	
J					
3	$(-)e$	—	a	—	s
2	$(+)e$	—	s	—	a
1	$(-)e$	—	a	—	s
0	$(+)e$	—	s	—	a

		$^1\Pi_g$		$^1\Pi_u$	
J					
3+	$(-)e$	—	a	—	s
−	$(+)f$	—	s	—	a
2+	$(+)e$	—	s	—	a
−	$(-)f$	—	a	—	s
1+	$(-)e$	—	a	—	s
−	$(+)f$	—	s	—	a

			$^3\Sigma_g^+$		$^3\Sigma_u^+$	
N	J					
	4	$(-)f$	—	a	—	s
3	3	$(-)e$	—	a	—	s
	2	$(-)f$	—	a	—	s
	3	$(+)f$	—	s	—	a
2	2	$(+)e$	—	s	—	a
	1	$(+)f$	—	s	—	a
	2	$(-)f$	—	a	—	s
1	1	$(-)e$	—	a	—	s
	0	$(-)f$	—	a	—	s
	1	$(+)f$	—	s	—	a
0						

			$^3\Pi_g$		$^3\Pi_u$	
			In	case	(a)	
J	Ω					
	2+	$(+)f$	—	s	—	a
	−	$(-)e$	—	a	—	s
3	1+	$(+)f$	—	s	—	a
	−	$(-)e$	—	a	—	s
	0+	$(+)f$	—	s	—	a
	−	$(-)e$	—	a	—	s
	2+	$(-)f$	—	a	—	s
	−	$(+)e$	—	s	—	a
2	1+	$(-)f$	—	a	—	s
	−	$(+)e$	—	s	—	a
	0+	$(-)f$	—	a	—	s
	−	$(+)e$	—	s	—	a
1	1+	$(+)f$	—	s	—	a
	−	$(-)e$	—	a	—	s
	0+	$(+)f$	—	s	—	a
	−	$(-)e$	—	a	—	s
0	0+	$(-)f$	—	a	—	s
	−	$(+)e$	—	s	—	a

2. Rotational Line Intensities

(A) Transformation between the Laboratory-Fixed System and the Molecule-Fixed System,

and the Rotational Wave Function. The spherical components of the laboratory-fixed coordinates $\boldsymbol{R}$ (X, Y, Z) and the molecule-fixed coordinates $\boldsymbol{r}$ (x, y, z) are defined as

$$\begin{aligned} R_{\pm 1} &= \mp(X \pm iY)/2^{1/2}, \quad R_0 = Z, \\ r_{\pm 1} &= \mp(x \pm iy)/2^{1/2}, \quad r_0 = z. \end{aligned} \tag{32}$$

The transformation between the laboratory-fixed system and the molecule-fixed system can be expressed by the rotation matrix D^J_{MN} (see Appendix A.3). The coordinates $\boldsymbol{R}$ and $\boldsymbol{r}$ are related by the following equations (see Appendix B):

$$\begin{aligned} R_\lambda &= \sum_{t=0,\pm 1} (-)^{\lambda - t} D^1_{-\lambda - t} r_t, \\ r_t &= \sum_{\lambda=0,\pm 1} D^1_{\lambda t} R_\lambda. \end{aligned} \tag{33}$$

The matrix element of the laboratory-fixed R_λ component of an electric dipole moment $\boldsymbol{\mu}$ can be calculated as

$$\begin{aligned} &< \Lambda S \Sigma v J \Omega M | \mu_{R_\lambda} | \Lambda' S' \Sigma' v' J' \Omega' M' > \\ &= \sum_{t=0,\pm 1} (-)^{\lambda - t} < v | < \Lambda | \mu_{r_t} | \Lambda' > | v' > \\ &\quad \times < S \Sigma | S' \Sigma' >< J \Omega M | D^1_{-\lambda - t} | J' \Omega' M' > \\ &= \sum_{t=0,\pm 1} (-)^{\lambda - t} < v | < \Lambda | \mu_{r_t} | \Lambda' > | v' > \\ &\quad \times \delta_{SS'} \delta_{\Sigma\Sigma'} (-)^{M' - \Omega'} [(2J+1)(2J'+1)]^{1/2} \\ &\quad \times \begin{pmatrix} J' & J & 1 \\ -M' & M & -\lambda \end{pmatrix} \begin{pmatrix} J' & J & 1 \\ -\Omega' & \Omega & -t \end{pmatrix}, \end{aligned} \tag{34}$$

where the last two factors with parentheses are the Wigner 3-j symbols.

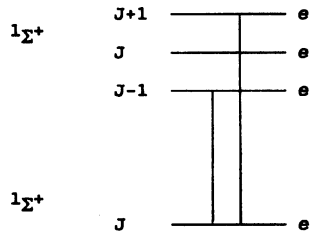
(B) Transition Dipole Moment between Rotational Levels.

i) $^1\Sigma^+$–$^1\Sigma^+$ Transition. The nonvanishing matrix elements of the transition dipole moment between $^1\Sigma^+$ and $^1\Sigma^+$ states are

$$\begin{aligned} &< {}^1\Sigma^+ v J M | \mu_{R_{-1}} | {}^1\Sigma^+ v' J+1 \; M+1 > \\ &\quad = -\mu_\parallel \left[\frac{(J+M+1)(J+M+2)}{2(2J+1)(2J+3)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_0} | {}^1\Sigma^+ v' J+1 \; M > \\ &\quad = \mu_\parallel \left[\frac{(J+M+1)(J-M+1)}{(2J+1)(2J+3)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_{+1}} | {}^1\Sigma^+ v' J+1 \; M-1 > \\ &\quad = -\mu_\parallel \left[\frac{(J-M+1)(J-M+2)}{2(2J+1)(2J+3)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_{-1}} | {}^1\Sigma^+ v' J-1 \; M+1 > \\ &\quad = \mu_\parallel \left[\frac{(J-M-1)(J-M)}{2(2J-1)(2J+1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_0} | {}^1\Sigma^+ v' J-1 \; M > \\ &\quad = \mu_\parallel \left[\frac{(J+M)(J-M)}{(2J-1)(2J+1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_{+1}} | {}^1\Sigma^+ v' J-1 \; M-1 > \\ &\quad = \mu_\parallel \left[\frac{(J+M-1)(J+M)}{2(2J-1)(2J+1)} \right]^{1/2}, \end{aligned} \tag{35}$$

where

$$\mu_\parallel = < v | < 0^+ | \mu_{r_0} | 0^+ > | v' > . \tag{36}$$

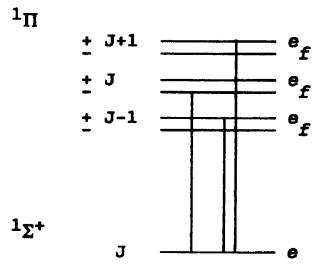


ii) $^1\Sigma^+$–$^1\Pi$ Transition. The nonvanishing matrix elements of the transition dipole moment between $^1\Sigma^+$ and $^1\Pi$ states are

$$\begin{aligned} &< {}^1\Sigma^+ v J M | \mu_{R_{-1}} | {}^1\Pi + v' J+1 \; M+1 > \\ &\quad = \mu_\perp \left[\frac{(J+2)(J+M+1)(J+M+2)}{2(J+1)(2J+3)(2J+1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_0} | {}^1\Pi + v' J+1 \; M > \\ &\quad = -\mu_\perp \left[\frac{(J+2)(J+M+1)(J-M+1)}{(J+1)(2J+3)(2J+1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_{+1}} | {}^1\Pi + v' J+1 \; M-1 > \\ &\quad = \mu_\perp \left[\frac{(J+2)(J-M+1)(J-M+2)}{2(J+1)(2J+3)(2J+1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_{-1}} | {}^1\Pi - v' J \; M+1 > \\ &\quad = \mu_\perp \left[\frac{(J+M+1)(J-M)}{2J(J+1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_0} | {}^1\Pi - v' J \; M > \\ &\quad = \mu_\perp M / [J(J+1)]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_{+1}} | {}^1\Pi - v' J \; M-1 > \\ &\quad = -\mu_\perp \left[\frac{(J+M)(J-M+1)}{2J(J+1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_{-1}} | {}^1\Pi + v' J-1 \; M+1 > \\ &\quad = \mu_\perp \left[\frac{(J-1)(J-M-1)(J-M)}{2J(2J+1)(2J-1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_0} | {}^1\Pi + v' J-1 \; M > \\ &\quad = \mu_\perp \left[\frac{(J-1)(J+M)(J-M)}{J(2J+1)(2J-1)} \right]^{1/2}, \\ &< {}^1\Sigma^+ v J M | \mu_{R_{+1}} | {}^1\Pi + v' J-1 \; M-1 > \\ &\quad = \mu_\perp \left[\frac{(J-1)(J+M)(J+M-1)}{2J(2J+1)(2J-1)} \right]^{1/2}, \end{aligned} \tag{37}$$

where

$$\begin{aligned} \mu_\perp &= < v | < 0^+ | \mu_{r_{-1}} | 1 > | v' > \\ &= < v | < 0^+ | \mu_{r_{+1}} | -1 > | v' > . \end{aligned} \tag{38}$$



iii) $^3\Sigma^+$–$^3\Sigma^+$ Transition. The nonvanishing matrix elements of the transition dipole moment between $^3\Sigma^+$ and $^3\Sigma^+$ states are

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+2J+1M+1> = -\mu_{\|}\left[\frac{(J+2)(J+M+1)(J+M+2)}{2(J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+2J+1M> = \mu_{\|}\left[\frac{(J+2)(J-M+1)(J+M+1)}{(J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+2J+1M-1> = -\mu_{\|}\left[\frac{(J+2)(J-M+1)(J-M+2)}{2(J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ+1M+1> = \mu_{\|}\frac{[(J+M+1)(J+M+2)/2]^{1/2}}{(J+1)(2J+1)(2J+3)},$$

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ+1M> = -\mu_{\|}\frac{[(J+M+1)(J-M+1)]^{1/2}}{(J+1)(2J+1)(2J+3)},$$

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ+1M-1> = \mu_{\|}\frac{[(J-M+1)(J-M+2)/2]^{1/2}}{(J+1)(2J+1)(2J+3)},$$

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ-1M+1> = \mu_{\|}\left[\frac{(J+1)(J-M-1)(J-M)}{2J(2J+1)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ-1M> = \mu_{\|}\left[\frac{(J+1)(J-M)(J+M)}{J(2J+1)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J+1JM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ-1M-1> = \mu_{\|}\left[\frac{(J+1)(J+M-1)(J+M)}{2J(2J+1)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+1J+1M+1> = -\mu_{\|}\left[\frac{J(J+2)(J+M+1)(J+M+2)}{2(J+1)^2(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+1J+1M> = \mu_{\|}\left[\frac{J(J+2)(J+M+1)(J-M+1)}{(J+1)^2(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+1J+1M-1> = -\mu_{\|}\left[\frac{J(J+2)(J-M+1)(J-M+2)}{2(J+1)^2(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+1JM+1> = \mu_{\|}[(J+M+1)(J-M)/2J(2J+1)]^{1/2}/(J+1),$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+1JM> = \mu_{\|}M/\left[J(J+1)^2(2J+1)\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+1JM-1> = -\mu_{\|}[(J-M+1)(J+M)/2J(2J+1)]^{1/2}/(J+1),$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-1JM+1> = \mu_{\|}[(J+M+1)(J-M)/2(J+1)(2J+1)]^{1/2}/J,$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-1JM> = \mu_{\|}M/\left[J^2(J+1)(2J+1)\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-1JM-1> = -\mu_{\|}[(J-M+1)(J+M)/2(J+1)(2J+1)]^{1/2}/J,$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-1J-1M+1> = \mu_{\|}\left[\frac{(J-1)(J+1)(J-M-1)(J-M)}{2(J)^2(2J-1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-1J-1M> = \mu_{\|}\left[\frac{(J-1)(J+1)(J+M)(J-M)}{(J)^2(2J-1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = JJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-1J-1M-1> = \mu_{\|}\left[\frac{(J-1)(J+1)(J+M-1)(J+M)}{2(J)^2(2J-1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ+1M+1> = -\mu_{\|}\left[\frac{J(J+M+1)(J+M+2)}{2(J+1)(2J+1)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ+1M> = \mu_{\|}\left[\frac{J(J-M+1)(J+M+1)}{(J+1)(2J+1)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ+1M-1> = -\mu_{\|}\left[\frac{J(J-M+1)(J-M+2)}{2(J+1)(2J+1)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ-1M+1> = -\mu_{\|}\frac{[(J-M-1)(J-M)/2]^{1/2}}{J(2J-1)(2J+1)},$$

$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ-1M> = -\mu_{\|}\frac{[(J+M)(J-M)]^{1/2}}{J(2J-1)(2J+1)},$$

$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ-1M-1> = -\mu_{\|}\frac{[(J+M-1)(J+M)/2]^{1/2}}{J(2J-1)(2J+1)},$$

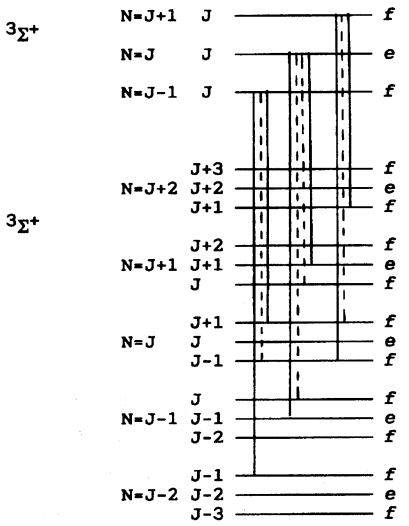
$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-2J-1M+1> = \mu_{\|}\left[\frac{(J-1)(J-M-1)(J-M)}{2J(2J-1)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-2J-1M> = \mu_{\|}\left[\frac{(J-1)(J-M)(J+M)}{J(2J-1)^2}\right]^{1/2},$$

$$< {}^3\Sigma^+ vN = J-1JM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-2J-1M-1> = \mu_{\|}\left[\frac{(J-1)(J+M-1)(J+M)}{2J(2J-1)^2}\right]^{1/2}, \quad (39)$$

where

$$\mu_{\|} = < v| < 0^+|\mu_{r_0}|0^+ > |v'> . \quad (40)$$



iv) $^3\Pi$–$^3\Sigma^+$ Transition. The nonvanishing matrix elements of the transition dipole moment between $^3\Pi$ (case(a)) and $^3\Sigma^+$ states are

$$< {}^3\Pi_0 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+2J+1\ M+1 > = \mu_\perp \left[\frac{(J+2)(J+M+1)(J+M+2)}{4(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+2J+1\ M > = -\mu_\perp \left[\frac{(J+2)(J-M+1)(J+M+1)}{2(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+2J+1\ M-1 > = \mu_\perp \left[\frac{(J+2)(J-M+1)(J-M+2)}{4(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+1J+1\ M+1 > = -\mu_\perp \left[\frac{(J+2)(J+M+1)(J+M+2)}{4(J+1)(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+1J+1\ M > = \mu_\perp \left[\frac{(J+2)(J-M+1)(J+M+1)}{2(J+1)(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+1J+1\ M-1 > = -\mu_\perp \left[\frac{(J+2)(J-M+1)(J-M+2)}{4(J+1)(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+1J\ M+1 > = -\mu_\perp \left[\frac{(J-M)(J+M+1)}{4(J+1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+1J\ M > = -\mu_\perp M/\left[2(J+1)(2J+1)\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+1J\ M-1 > = \mu_\perp \left[\frac{(J+M)(J-M+1)}{4(J+1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ+1\ M+1 > = \mu_\perp \frac{(J+2)}{2(2J+3)}\left[\frac{(J+M+1)(J+M+2)}{(J+1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ+1\ M > = -\mu_\perp \frac{(J+2)}{(2J+3)}\left[\frac{(J-M+1)(J+M+1)}{2(J+1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ+1\ M-1 > = \mu_\perp \frac{(J+2)}{2(2J+3)}\left[\frac{(J-M+1)(J-M+2)}{(J+1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J\,J\ M+1 > = \mu_\perp \left[\frac{(J-M)(J+M+1)}{4J(J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J\,J\ M > = \mu_\perp M/\left[2J(J+1)\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J\,J\ M-1 > = -\mu_\perp \left[\frac{(J+M)(J-M+1)}{4J(J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ-1\ M+1 > = \mu_\perp \frac{(J-1)}{2(2J-1)}\left[\frac{(J-M-1)(J-M)}{J(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ-1\ M > = \mu_\perp \frac{(J-1)}{(2J-1)}\left[\frac{(J-M)(J+M)}{2J(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ-1\ M-1 > = \mu_\perp \frac{(J-1)}{2(2J-1)}\left[\frac{(J+M-1)(J+M)}{J(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-1J\ M+1 > = -\mu_\perp \left[\frac{(J-M)(J+M+1)}{4J(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-1J\ M > = -\mu_\perp M/\left[2J(2J+1)\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-1J\ M-1 > = \mu_\perp \left[\frac{(J+M)(J-M+1)}{4J(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-1J-1\ M+1 > = -\mu_\perp \left[\frac{(J-1)(J-M-1)(J-M)}{4J(2J-1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-1J-1\ M > = -\mu_\perp \left[\frac{(J-1)(J-M)(J+M)}{2J(2J-1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-1J-1\ M-1 > = -\mu_\perp \left[\frac{(J-1)(J+M-1)(J+M)}{4J(2J-1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-2J-1\ M+1 > = \mu_\perp \left[\frac{(J-1)(J-M-1)(J-M)}{4(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-2J-1\ M > = \mu_\perp \left[\frac{(J-1)(J-M)(J+M)}{2(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_0 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-2J-1\ M-1 > = \mu_\perp \left[\frac{(J-1)(J+M-1)(J+M)}{4(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+2J+1\ M+1 > = -\mu_\perp \left[\frac{J(J+2)(J+M+1)(J+M+2)}{2(J+1)(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+2J+1\ M >$$

$$= \mu_\perp \left[\frac{J(J+2)(J-M+1)(J+M+1)}{(J+1)(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+2J+1\ M-1 >$$
$$= -\mu_\perp \left[\frac{J(J+2)(J-M+1)(J-M+2)}{2(J+1)(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_1 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+1J\ M+1 >$$
$$= \mu_\perp \left[\frac{(J-M)(J+M+1)}{2J(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+1J\ M >$$
$$= \mu_\perp M/\left[J(2J+1)\right]^{1/2},$$

$$< {}^3\Pi_1 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+1J\ M-1 >$$
$$= -\mu_\perp \left[\frac{(J+M)(J-M+1)}{2J(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ+1\ M+1 >$$
$$= -\mu_\perp \left[\frac{J(J+M+1)(J+M+2)}{2(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ+1\ M >$$
$$= \mu_\perp \left[\frac{J(J-M+1)(J+M+1)}{(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ+1\ M-1 >$$
$$= -\mu_\perp \left[\frac{J(J-M+1)(J-M+2)}{2(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ-1\ M+1 >$$
$$= -\mu_\perp \left[\frac{(J+1)(J-M-1)(J-M)}{2(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ-1\ M >$$
$$= -\mu_\perp \left[\frac{(J+1)(J-M)(J+M)}{(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ-1\ M-1 >$$
$$= -\mu_\perp \left[\frac{(J+1)(J+M-1)(J+M)}{2(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-1J\ M+1 >$$
$$= -\mu_\perp \left[\frac{(J-M)(J+M+1)}{2(J+1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-1J\ M >$$
$$= -\mu_\perp M/\left[(J+1)(2J+1)\right]^{1/2},$$

$$< {}^3\Pi_1 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-1J\ M-1 >$$
$$= \mu_\perp \left[\frac{(J+M)(J-M+1)}{2(J+1)(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-2J-1\ M+1 >$$
$$= \mu_\perp \left[\frac{(J-1)(J+1)(J-M-1)(J-M)}{2J(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-2J-1\ M >$$
$$= \mu_\perp \left[\frac{(J-1)(J+1)(J-M)(J+M)}{J(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_1 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-2J-1\ M-1 >$$
$$= \mu_\perp \left[\frac{(J-1)(J+1)(J+M-1)(J+M)}{2J(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+2J+1M+1 >$$
$$= \mu_\perp \left[\frac{J(J-1)(J+M+1)(J+M+2)}{4(J+1)(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+2J+1M >$$
$$= -\mu_\perp \left[\frac{J(J-1)(J-M+1)(J+M+1)}{2(J+1)(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+2J+1M-1 >$$
$$= \mu_\perp \left[\frac{J(J-1)(J-M+1)(J-M+2)}{4(J+1)(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+1J+1M+1 >$$
$$= \mu_\perp \left[\frac{J(J-1)(J+M+1)(J+M+2)}{4(J+1)^2(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Pi_2 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+1J+1M >$$
$$= -\mu_\perp \left[\frac{J(J-1)(J-M+1)(J+M+1)}{2(J+1)^2(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Pi_2 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+1J+1M-1 >$$
$$= \mu_\perp \left[\frac{J(J-1)(J-M+1)(J-M+2)}{4(J+1)^2(2J+1)(2J+3)}\right]^{1/2},$$

$$< {}^3\Pi_2 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J+1J\ M+1 >$$
$$= -\mu_\perp \left[\frac{(J-1)(J+2)(J-M)(J+M+1)}{4J(J+1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_2 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J+1J\ M >$$
$$= -\mu_\perp M \left[\frac{(J-1)(J+2)}{2J(J+1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_2 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J+1J\ M-1 >$$
$$= \mu_\perp \left[\frac{(J-1)(J+2)(J+M)(J-M+1)}{4J(J+1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ+1M+1 >$$
$$= \mu_\perp \left[\frac{J(J-1)(J+2)(J+M+1)(J+M+2)}{4(J+1)^2(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ+1M >$$
$$= -\mu_\perp \left[\frac{J(J-1)(J+2)(J-M+1)(J+M+1)}{2(J+1)^2(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ+1M-1 >$$
$$= \mu_\perp \left[\frac{J(J-1)(J+2)(J-M+1)(J-M+2)}{4(J+1)^2(2J+1)(2J+3)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J\ J\ M+1 >$$
$$= -\mu_\perp \left[\frac{(J-1)(J+2)(J-M)(J+M+1)}{4J^2(J+1)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J\ J\ M >$$
$$= -\mu_\perp M \left[\frac{(J-1)(J+2)}{2J^2(J+1)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J\ J\ M-1 >$$
$$= \mu_\perp \left[\frac{(J-1)(J+2)(J+M)(J-M+1)}{4J^2(J+1)^2}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = JJ-1M+1 >$$
$$= \mu_\perp \left[\frac{(J-1)(J+1)(J+2)(J-M-1)(J-M)}{4J^2(2J-1)^2(2J+1)}\right]^{1/2},$$

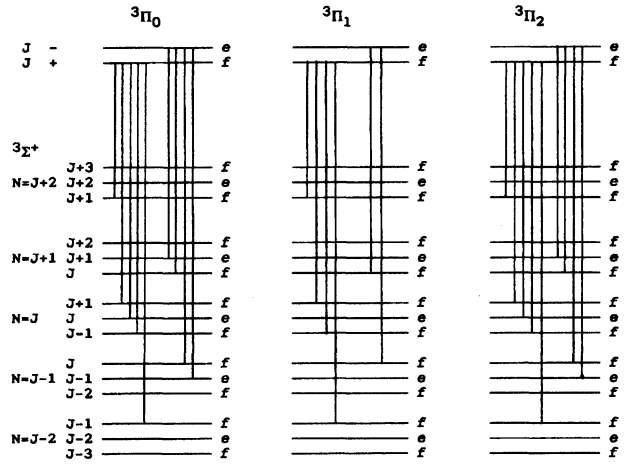
$$< {}^3\Pi_2 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = JJ-1M >$$
$$= \mu_\perp \left[\frac{(J-1)(J+1)(J+2)(J-M)(J+M)}{2J^2(2J-1)^2(2J+1)}\right]^{1/2},$$

$$< {}^3\Pi_2 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = JJ-1M-1 >$$
$$= \mu_\perp \left[\frac{(J-1)(J+1)(J+2)(J+M-1)(J+M)}{4J^2(2J-1)^2(2J+1)}\right]^{1/2},$$

$$
\begin{aligned}
&<{}^3\Pi_2 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-1\, J\, M+1> \\
&\quad = -\mu_\perp \left[\frac{(J-1)(J+2)(J-M)(J+M+1)}{4J^2(J+1)(2J+1)}\right]^{1/2}, \\
&<{}^3\Pi_2 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-1\, J\, M> \\
&\quad = -\mu_\perp M \left[\frac{(J-1)(J+2)}{2J^2(J+1)(2J+1)}\right]^{1/2}, \\
&<{}^3\Pi_2 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-1\, J\, M-1> \\
&\quad = \mu_\perp \left[\frac{(J-1)(J+2)(J+M)(J-M+1)}{4J^2(J+1)(2J+1)}\right]^{1/2}, \\
&<{}^3\Pi_2 - vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-1\, J-1\, M+1> \\
&\quad = \mu_\perp \left[\frac{(J+1)(J+2)(J-M)(J-M-1)}{4J^2(2J+1)(2J-1)}\right]^{1/2}, \\
&<{}^3\Pi_2 - vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-1\, J-1\, M> \\
&\quad = \mu_\perp \left[\frac{(J+1)(J+2)(J-M)(J+M)}{2J^2(2J+1)(2J-1)}\right]^{1/2}, \\
&<{}^3\Pi_2 - vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-1\, J-1\, M-1> \\
&\quad = \mu_\perp \left[\frac{(J+1)(J+2)(J+M)(J+M-1)}{4J^2(2J-1)(2J+1)}\right]^{1/2}, \\
&<{}^3\Pi_2 + vJM|\mu_{R_{-1}}|{}^3\Sigma^+ v'N = J-2\, J-1\, M+1> \\
&\quad = \mu_\perp \left[\frac{(J+1)(J+2)(J-M-1)(J-M)}{4J(2J+1)(2J-1)^2}\right]^{1/2}, \\
&<{}^3\Pi_2 + vJM|\mu_{R_0}|{}^3\Sigma^+ v'N = J-2\, J-1\, M> \\
&\quad = \mu_\perp \left[\frac{(J+1)(J+2)(J-M)(J+M)}{2J(2J-1)^2(2J+1)}\right]^{1/2}, \\
&<{}^3\Pi_2 + vJM|\mu_{R_{+1}}|{}^3\Sigma^+ v'N = J-2\, J-1\, M-1> \\
&\quad = \mu_\perp \left[\frac{(J+1)(J+2)(J+M-1)(J+M)}{4J(2J-1)^2(2J+1)}\right]^{1/2}, \qquad (41)
\end{aligned}
$$

where

$$
\begin{aligned}
\mu_\perp &= <v|<1|\mu_{r_{+1}}|0^+>|v'> \\
&= <v|<-1|\mu_{r_{-1}}|0^+>|v'>. \qquad (42)
\end{aligned}
$$



(C) Selection Rules. The selection rules for the matrix elements of the electric dipole moment are[3]

$$\Delta J = 0,\ \pm 1 \text{ with the restriction } J = 0 \not\longleftrightarrow J = 0,$$
$$(+) \longleftrightarrow (-)\ (e \longleftrightarrow f \text{ for } \Delta J = 0,\ e \longleftrightarrow e \text{ and } f \longleftrightarrow f \text{ for } \Delta J = \pm 1),$$
$$s \longleftrightarrow s,\ a \longleftrightarrow a,\ \mathrm{g} \longleftrightarrow \mathrm{u}.$$

In Hund's cases (a) and (b)

$$\Delta\Omega = 0,\ \pm 1,$$
$$\Sigma^+ \longleftrightarrow \Sigma^+,\ \Sigma^- \longleftrightarrow \Sigma^-,\ \Delta S = 0.$$

3. Spin–Orbit Interaction

(A) Matrix Elements of Spin–Orbit Interaction. The spin–orbit Hamiltonian of Eq. 7 can be written as

$$H_{\mathrm{so}} = \sum_i \xi(r_i)[(l_{+i}s_{-i} + l_{-i}s_{+i})/2 + l_{zi}s_{zi}]. \qquad (43)$$

The matrix elements of H_{so} for various electron configurations were calculated by Kovàcs.[13] Let us calculate the spin–orbit matrix elements for the electronic states of group [B] expressed by Eq. 10. Only the states having the same g or u symmetry can interact. By omitting the suffixes g and u, we shall use the following configuration representation for the electronic states of group [B].

$$
\begin{aligned}
|{}^1\Sigma^+\ 0^+> &= |0^+>|0\ \ 0> \\
&= (2)^{-1/2}[|(\sigma s)(\overline{\sigma p_0})| - |(\overline{\sigma s})(\sigma p_0)|], \\
|{}^3\Sigma^+ + 1> &= |0^+>|1\ \ 1> = |(\sigma s)(\sigma p_0)|, \\
|{}^3\Sigma^+ - 1> &= |0^+>|1\ -1> = |(\overline{\sigma s})(\overline{\sigma p_0})|, \\
|{}^3\Sigma^+\ 0^-> &= |0^+>|1\ \ 0> \\
&= (2)^{-1/2}[|(\sigma s)(\overline{\sigma p_0})| + |(\overline{\sigma s})(\sigma p_0)|], \\
|{}^1\Pi\ +1> &= |+1>|0\ \ 0> \\
&= (2)^{-1/2}[|(\sigma s)(\overline{\pi p_{+1}})| - |(\overline{\sigma s})(\pi p_{+1})|], \\
|{}^1\Pi\ -1> &= |-1>|0\ \ 0> \\
&= (2)^{-1/2}[|(\sigma s)(\overline{\pi p_{-1}})| - |(\overline{\sigma s})(\pi p_{-1})|], \\
|{}^3\Pi\ +2> &= |+1>|1\ \ 1> = |(\sigma s)(\pi p_{+1})|, \\
|{}^3\Pi\ \ 0'> &= |+1>|1\ -1> = |(\overline{\sigma s})(\overline{\pi p_{+1}})|, \\
|{}^3\Pi\ \ 0''> &= |-1>|1\ \ 1> = |(\sigma s)(\pi p_{-1})|, \\
|{}^3\Pi\ -2> &= |-1>|1\ -1> = |(\overline{\sigma s})(\overline{\pi p_{-1}})|, \\
|{}^3\Pi\ +1> &= |+1>|1\ \ 0> \\
&= (2)^{-1/2}[|(\sigma s)(\overline{\pi p_{+1}})| + |(\overline{\sigma s})(\pi p_{+1})|], \\
|{}^3\Pi\ -1> &= |-1>|1\ \ 0> \\
&= (2)^{-1/2}[|(\sigma s)(\overline{\pi p_{-1}})| + |(\overline{\sigma s})(\pi p_{-1})|]. \qquad (44)
\end{aligned}
$$

For one electron operators l_+, l_-, l_z, s_+, s_-, and s_z,

$$
\begin{aligned}
&l_+|p_0> = (2)^{1/2}|p_{+1}>,\ l_-|p_{+1}> = (2)^{1/2}|p_0>, \\
&l_z|p_{+1}> = +|p_{+1}>,\ l_+|p_{-1}> = (2)^{1/2}|p_0>, \\
&l_-|p_0> = (2)^{1/2}|p_{-1}>,\ l_z|p_{-1}> = -|p_{-1}>, \\
&s_+|1/2\ -1/2> = |1/2\ \ 1/2>, \\
&s_-|1/2\ \ 1/2> = |1/2\ -1/2>, \\
&s_z|1/2\ -1/2> = -1/2|1/2\ -1/2>, \\
&s_z|1/2\ \ 1/2> = 1/2|1/2\ \ 1/2>. \qquad (45)
\end{aligned}
$$

The nonvanishing matrix elements for the electronic wave functions of Eq. 44 are

$$
\begin{aligned}
&<{}^1\Sigma^+\ 0^+|H_{so}|{}^3\Pi\ \ 0'>=<{}^3\Pi\ 0'|H_{so}|{}^1\Sigma^+\ 0^+>=-C,\\
&<{}^1\Sigma^+\ 0^+|H_{so}|{}^3\Pi\ \ 0''>=<{}^3\Pi\ 0''|H_{so}|{}^1\Sigma^+\ 0^+>=C,\\
&<{}^3\Sigma^+ + 1|H_{so}|{}^1\Pi + 1>=<{}^1\Pi + 1|H_{so}|{}^3\Sigma^+ + 1>=C,\\
&<{}^3\Sigma^+ + 1|H_{so}|{}^3\Pi + 1>=<{}^3\Pi + 1|H_{so}|{}^3\Sigma^+ + 1>=C,\\
&<{}^3\Sigma^+ - 1|H_{so}|{}^1\Pi - 1>=<{}^1\Pi - 1|H_{so}|{}^3\Sigma^+ - 1>=-C,\\
&<{}^3\Sigma^+ - 1|H_{so}|{}^3\Pi - 1>=<{}^3\Pi - 1|H_{so}|{}^3\Sigma^+ - 1>=C,\\
&<{}^3\Sigma^+\ 0^-|H_{so}|{}^3\Pi\ \ 0'>=<{}^3\Pi\ 0'|H_{so}|{}^3\Sigma^+\ 0^->=C,\\
&<{}^3\Sigma^+\ 0^-|H_{so}|{}^3\Pi\ \ 0''>=<{}^3\Pi\ 0''|H_{so}|{}^3\Sigma^+\ 0^->=C,\\
&<{}^1\Pi + 1|H_{so}|{}^3\Pi + 1>=<{}^3\Pi + 1|H_{so}|{}^1\Pi + 1>=-C,\\
&<{}^1\Pi - 1|H_{so}|{}^3\Pi - 1>=<{}^3\Pi - 1|H_{so}|{}^1\Pi - 1>=C,\\
&<{}^3\Pi + 2|H_{so}|{}^3\Pi + 2>=C,\\
&<{}^3\Pi\ \ 0'\ |H_{so}|{}^3\Pi\ \ 0'>=-C,\\
&<{}^3\Pi\ \ 0''|H_{so}|{}^3\Pi\ \ 0''>=-C,\\
&<{}^3\Pi\ -2|H_{so}|{}^3\Pi - 2>=C,
\end{aligned}
\tag{46}
$$

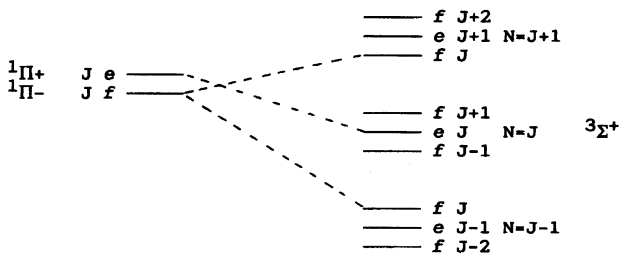
where, by neglecting two center integrals,

$$
\begin{aligned}
C &= <(\sigma p_0)|\xi(r)|(\sigma p_0)>/2 = <(\pi p_{\pm 1})|\xi(r)|(\pi p_{\pm 1})>/2\\
&= <np_x^A|\xi(r)|np_x^A>/2 = <np_y^A|\xi(r)|np_y^A>/2\\
&= <np_z^A|\xi(r)|np_z^A>/2.
\end{aligned}
\tag{47}
$$

Nonvanishing matrix elements of the spin–orbit perturbation between the eigenfunctions (15), (18), (21), and (24) are as follows.

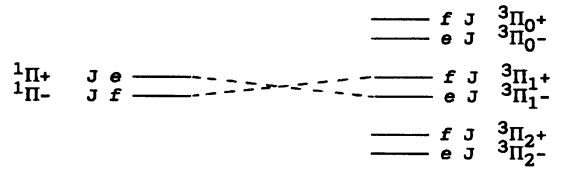
i) $^1\Pi$–$^3\Sigma^+$ Perturbation.

$$
\begin{aligned}
&<{}^1\Pi - vJM|H_{so}|{}^3\Sigma^+ v'N = J + 1JM>\\
&\quad = [J/(2J+1)]^{1/2}C<v|v'>,\\
&<{}^1\Pi - vJM|H_{so}|{}^3\Sigma^+ v'N = J - 1JM>\\
&\quad = [(J+1)/(2J+1)]^{1/2}C<v|v'>,\\
&<{}^1\Pi + vJM|H_{so}|{}^3\Sigma^+ v'N = JJM>\\
&\quad = C<v|v'>.
\end{aligned}
\tag{48}
$$



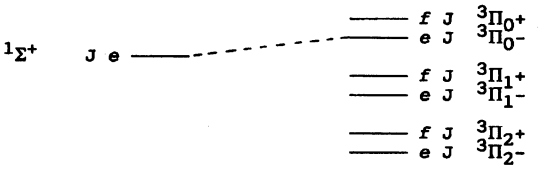
ii) $^1\Pi$–$^3\Pi$ Perturbation.

$$
\begin{aligned}
&<{}^1\Pi + vJM|H_{so}|{}^3\Pi_1 - v'JM> = -C<v|v'>,\\
&<{}^1\Pi - vJM|H_{so}|{}^3\Pi_1 + v'JM> = -C<v|v'>.
\end{aligned}
\tag{49}
$$



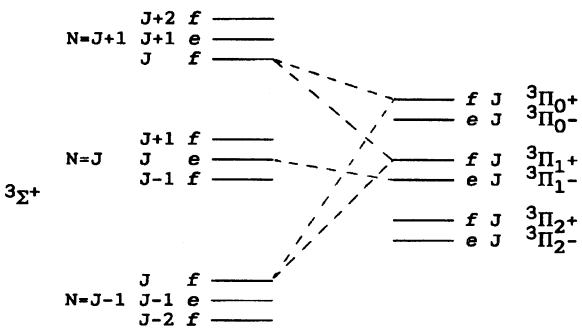
iii) $^1\Sigma^+$–$^3\Pi$ Perturbation.

$$
<{}^1\Sigma^+ vJM|H_{so}|{}^3\Pi_0 - v'JM> = -(2)^{1/2}C<v|v'>. \tag{50}
$$



iv) $^3\Sigma^+$–$^3\Pi$ Perturbation.

$$
\begin{aligned}
&<{}^3\Sigma^+ vN = J + 1JM|H_{so}|{}^3\Pi_1 + v'JM>\\
&\quad = [J/(2J+1)]^{1/2}C<v|v'>,\\
&<{}^3\Sigma^+ vN = J - 1JM|H_{so}|{}^3\Pi_1 + v'JM>\\
&\quad = [(J+1)/(2J+1)]^{1/2}C<v|v'>,\\
&<{}^3\Sigma^+ vN = JJM|H_{so}|{}^3\Pi_1 - v'JM>\\
&\quad = C<v|v'>,\\
&<{}^3\Sigma^+ vN = J + 1JM|H_{so}|{}^3\Pi_0 + v'JM>\\
&\quad = -[2(J+1)/(2J+1)]^{1/2}C<v|v'>,\\
&<{}^3\Sigma^+ vN = J - 1JM|H_{so}|{}^3\Pi_0 + v'JM>\\
&\quad = [2J/(2J+1)]^{1/2}C<v|v'>.
\end{aligned}
\tag{51}
$$



At the limit of $R \to \infty$, the diagonal term energies are degenerate, and the matrix is

	$^1\Sigma^+$ 0^+	$^3\Sigma^+$ 0^-	$^3\Pi$ $0'$	$^3\Pi$ $0''$	$^3\Sigma^+$ $+1$	$^1\Pi$ $+1$	$^3\Pi$ $+1$	$^3\Sigma^+$ -1	$^1\Pi$ -1	$^3\Pi$ -1	$^3\Pi$ $+2$	$^3\Pi$ -2
$^1\Sigma^+$ 0^+	0	0	$-C$	C	0	0	0	0	0	0	0	0
$^3\Sigma^+$ 0^-	0	0	C	C	0	0	0	0	0	0	0	0
$^3\Pi$ $0'$	$-C$	C	$-C$	0	0	0	0	0	0	0	0	0
$^3\Pi$ $0''$	C	C	0	$-C$	0	0	0	0	0	0	0	0
$^3\Sigma^+$ $+1$	0	0	0	0	0	C	C	0	0	0	0	0
$^1\Pi$ $+1$	0	0	0	0	C	0	$-C$	0	0	0	0	0
$^3\Pi$ $+1$	0	0	0	0	C	$-C$	0	0	0	0	0	0
$^3\Sigma^+$ -1	0	0	0	0	0	0	0	0	$-C$	C	0	0
$^1\Pi$ -1	0	0	0	0	0	0	0	$-C$	0	C	0	0
$^3\Pi$ -1	0	0	0	0	0	0	0	C	C	0	0	0
$^3\Pi$ $+2$	0	0	0	0	0	0	0	0	0	0	C	0
$^3\Pi$ -2	0	0	0	0	0	0	0	0	0	0	0	C

(52)

The eigenfunctions for eigenvalue$=C$ are

$$
\begin{aligned}
&|^3\Pi \pm 2>,\\
&(2)^{-1/2}(|^3\Pi \pm 1> \mp |^1\Pi \pm 1>),\\
&(6)^{-1/2}(2|^3\Sigma^+ \pm 1> + |^3\Pi \pm 1> \pm |^1\Pi \pm 1>),\\
&(6)^{-1/2}(2|^3\Sigma^+\ 0^-> + |^3\Pi\ 0'> + |^3\Pi\ 0''>),\\
&(6)^{-1/2}(2|^1\Sigma^+\ 0^+> - |^3\Pi\ 0'> + |^3\Pi\ 0''>). \qquad (53)
\end{aligned}
$$

The eigenfunctions for eigenvalue$=-2C$ are

$$
\begin{aligned}
&(3)^{-1/2}(|^3\Sigma^+ \pm 1> - |^3\Pi \pm 1> \mp |^1\Pi \pm 1>),\\
&(3)^{-1/2}(|^3\Sigma^+\ 0^-> - |^3\Pi\ 0'> - |^3\Pi\ 0''>),\\
&(3)^{-1/2}(|^1\Sigma^+\ 0^+> + |^3\Pi\ 0'> - |^3\Pi\ 0''>). \qquad (54)
\end{aligned}
$$

Let us calculate the spin–orbit matrix elements for the electronic states of group [C] expressed by Eq. 11. We shall use the following configuration representation for the electronic states of group [C].

$$
\begin{aligned}
|^1\Sigma^+\ 0^+> &= |0^+>|0\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\sigma d_0})| - |(\overline{\sigma s})(\sigma d_0)|],\\
|^3\Sigma^+ +1> &= |0^+>|1\ \ 1> = |(\sigma s)(\sigma d_0)|,\\
|^3\Sigma^+ -1> &= |0^+>|1\ -1> = |(\overline{\sigma s})(\overline{\sigma d_0})|,\\
|^3\Sigma^+\ 0^-> &= |0^+>|1\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\sigma d_0})| + |(\overline{\sigma s})(\sigma d_0)|],\\
|^1\Pi\ +1> &= |+1>|0\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\pi d_{+1}})| - |(\overline{\sigma s})(\pi d_{+1})|],\\
|^1\Pi\ -1> &= |-1>|0\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\pi d_{-1}})| - |(\overline{\sigma s})(\pi d_{-1})|],\\
|^3\Pi\ +2> &= |+1>|1\ \ 1> = |(\sigma s)(\pi d_{+1})|,\\
|^3\Pi\ 0'> &= |+1>|1\ -1> = |(\overline{\sigma s})(\overline{\pi d_{+1}})|,\\
|^3\Pi\ 0''> &= |-1>|1\ \ 1> = |(\sigma s)(\pi d_{-1})|,\\
|^3\Pi\ -2> &= |-1>|1\ -1> = |(\overline{\sigma s})(\overline{\pi d_{-1}})|,\\
|^3\Pi\ +1> &= |+1>|1\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\pi d_{+1}})| + |(\overline{\sigma s})(\pi d_{+1})|],\\
|^3\Pi\ -1> &= |-1>|1\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\pi d_{-1}})| + |(\overline{\sigma s})(\pi d_{-1})|],\\
|^1\Delta\ +2> &= |+2>|0\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\delta d_{+2}})| - |(\overline{\sigma s})(\delta d_{+2})|],\\
|^1\Delta\ -2> &= |-2>|0\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\delta d_{-2}})| - |(\overline{\sigma s})(\delta d_{-2})|],\\
|^3\Delta\ +3> &= |+2>|1\ \ 1> = |(\sigma s)(\delta d_{+2})|,\\
|^3\Delta +1> &= |+2>|1\ -1> = |(\overline{\sigma s})(\overline{\delta d_{+2}})|,\\
|^3\Delta\ -1> &= |-2>|1\ \ 1> = |(\sigma s)(\delta d_{-2})|,\\
|^3\Delta -3> &= |-2>|1\ -1> = |(\overline{\sigma s})(\overline{\delta d_{-2}})|,\\
|^3\Delta\ +2> &= |+2>|1\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\delta d_{+2}})| + |(\overline{\sigma s})(\delta d_{+2})|],\\
|^3\Delta\ -2> &= |-2>|1\ \ 0>\\
&= (2)^{-1/2}[|(\sigma s)(\overline{\delta d_{-2}})| + |(\overline{\sigma s})(\delta d_{-2})|]. \qquad (55)
\end{aligned}
$$

For one electron operators l_+, l_-, and l_z,

$$
\begin{aligned}
&l_+|d_{+1}> = 2|d_{+2}>,\ l_-|d_{+2}> = 2|d_{+1}>,\\
&l_z|d_{+2}> = +2|d_{+2}>,\\
&l_+|d_0> = (6)^{1/2}|d_{+1}>,\ l_-|d_{+1}> = (6)^{1/2}|d_0>,\\
&l_z|d_{+1}> = +1|d_{+1}>,\\
&l_+|d_{-1}> = (6)^{1/2}|d_0>,\ l_-|d_0> = (6)^{1/2}|d_{-1}>,\\
&l_z|d_{-1}> = -1|d_{-1}>,\\
&l_+|d_{-2}> = 2|d_{-1}>,\ l_-|d_{-1}> = 2|d_{-2}>,\\
&l_z|d_{-2}> = -2|d_{-2}>. \qquad (56)
\end{aligned}
$$

The nonvanishing symmetric matrix elements for the electronic wave functions of Eq. 55 are

$$
\begin{aligned}
&<^1\Sigma^+\ 0^+|H_{so}|^3\Pi\ 0'> = -D,\\
&<^1\Sigma^+\ 0^+|H_{so}|^3\Pi\ 0''> = D,\\
&<^3\Sigma^+ +1|H_{so}|^1\Pi +1> = D,\\
&<^3\Sigma^+ +1|H_{so}|^3\Pi +1> = D,\\
&<^3\Sigma^+ -1|H_{so}|^1\Pi -1> = -D,\\
&<^3\Sigma^+ -1|H_{so}|^3\Pi -1> = D,\\
&<^3\Sigma^+\ 0^-|H_{so}|^3\Pi\ 0'> = D,\\
&<^3\Sigma^+\ 0^-|H_{so}|^3\Pi\ 0''> = D,\\
&<^1\Pi +1|H_{so}|^3\Pi +1> = -E,\\
&<^1\Pi -1|H_{so}|^3\Pi -1> = E,\\
&<^3\Pi\ 0'|H_{so}|^3\Pi\ 0'> = -E,\\
&<^3\Pi\ 0''|H_{so}|^3\Pi\ 0''> = -E,\\
&<^3\Pi +2|H_{so}|^3\Pi +2> = E,\\
&<^3\Pi -2|H_{so}|^3\Pi -2> = E,\\
&<^1\Pi +1|H_{so}|^3\Delta +1> = -(2)^{1/2}E,\\
&<^1\Pi -1|H_{so}|^3\Delta -1> = (2)^{1/2}E,\\
&<^3\Pi +1|H_{so}|^3\Delta +1> = (2)^{1/2}E,\\
&<^3\Pi -1|H_{so}|^3\Delta -1> = (2)^{1/2}E,\\
&<^3\Pi +2|H_{so}|^3\Delta +2> = (2)^{1/2}E,\\
&<^3\Pi -2|H_{so}|^3\Delta -2> = (2)^{1/2}E,\\
&<^1\Delta +2|H_{so}|^3\Delta +2> = -F,\\
&<^1\Delta -2|H_{so}|^3\Delta -2> = F,
\end{aligned}
$$

$$
\begin{aligned}
&< {}^3\Delta + 1|H_{so}|{}^3\Delta + 1 >= -F,\\
&< {}^3\Delta - 1|H_{so}|{}^3\Delta - 1 >= -F,\\
&< {}^3\Delta + 3|H_{so}|{}^3\Delta + 3 >= F,\\
&< {}^3\Delta - 3|H_{so}|{}^3\Delta - 3 >= F,
\end{aligned} \tag{57}
$$

where

$$
\begin{aligned}
D &= < (\sigma d_0)|\xi(r)|(\sigma d_0) > (3)^{1/2}/2,\\
E &= < (\pi d_{\pm 1})|\xi(r)|(\pi d_{\pm 1}) > /2,\\
F &= < (\delta d_{\pm 2})|\xi(r)|(\delta d_{\pm 2}) > .
\end{aligned} \tag{58}
$$

The nonvanishing matrix elements between the electronic wave functions of ${}^3\Sigma^+$ state in group [B] and those of Eq. 55 in group [C] are

$$
\begin{aligned}
&< {}^3\Sigma^+ + 1|H_{so}|{}^1\Pi + 1 >= G,\\
&< {}^3\Sigma^+ - 1|H_{so}|{}^1\Pi - 1 >= -G,\\
&< {}^3\Sigma^+ + 1|H_{so}|{}^3\Pi + 1 >= G,\\
&< {}^3\Sigma^+ - 1|H_{so}|{}^3\Pi - 1 >= G,\\
&< {}^3\Sigma^+ \ 0^-|H_{so}|{}^3\Pi \ 0' >= G,\\
&< {}^3\Sigma^+ \ 0^-|H_{so}|{}^3\Pi \ 0'' >= G,
\end{aligned} \tag{59}
$$

where

$$
G =< (\sigma p_0)|\xi(r)|(\sigma d_0) > (3)^{1/2}/2. \tag{60}
$$

(B) Selection Rules. The selection rules for the spin–orbit perturbation are[3]

$$
\begin{aligned}
&\Delta J = 0,\ \Delta\Omega = 0,\ \mathrm{g} \longleftrightarrow \mathrm{g} \text{ and } \mathrm{u} \longleftrightarrow \mathrm{u},\\
&(+) \longleftrightarrow (+) \text{ and } (-) \longleftrightarrow (-)\\
&(e \longleftrightarrow e \text{ and } f \longleftrightarrow f),\ \Sigma^+ \longleftrightarrow \Sigma^-,\\
&\Delta S = 0,\ \pm 1 \text{ and } \Delta\Lambda = -\Delta\Sigma = 0,\ \pm 1.
\end{aligned}
$$

In the single-configuration limit, if the two interacting states belong to the same configuration, $\Delta\Lambda=\Delta\Sigma=0$, and if the two interacting states differ by at most one spin–orbital, $\Delta\Lambda=-\Delta\Sigma=\pm 1$.

4. Rotational Interaction

There are three terms in the rotational part of the Hamiltonian of Eq. 2 which are neglected in the Born–Oppenheimer approximation:

$$
\begin{aligned}
H_{SL} &= B(L_+S_- + L_-S_+),\\
H_{JS} &= -B(J_+S_- + J_-S_+),\\
H_{JL} &= -B(J_+L_- + J_-L_+).
\end{aligned} \tag{61}
$$

H_{SL} causes spin-electronic *homogeneous* ($\Delta\Omega=0$) perturbations. The S-uncoupling operator H_{JS} and the L-uncoupling operator H_{JL} give rise to *heterogeneous* ($\Delta\Omega=\pm 1$) perturbations. Uncoupling of the electron spin angular momentum or uncoupling of the electron orbital angular momentum from the internuclear axis occurs because of rotation. These uncoupling phenomena can be attributed to Coriolis interaction in the rotating molecule. The interaction matrix element of a homogeneous ($\Delta\Omega=0$) perturbation is independent on J, but the one of a heterogeneous ($\Delta\Omega=\pm 1$) perturbation depends on J.

(A) Spin–Electronic Interaction. For the off-diagonal elements of $B(L_+S_-+L_-S_+)$, the selection rules $\Delta\Omega=0$, $\Delta\Lambda=-\Delta\Sigma=\pm 1$ are the same as those for the part of the spin–orbit interaction $\sum_i\xi_i(l_{+i}s_{-i}+l_{-i}s_{+i})$ except that $\Delta S=0$ only for H_{SL}. The nonzero matrix elements are

$$
\begin{aligned}
&< J\Omega M| < v| < S\Sigma - 1| < \Lambda + 1|B(L_+S_-\\
&\quad +L_-S_+)|\Lambda > |S\Sigma > |v' > |J\Omega M >\\
&\quad =< v|B|v' >< \Lambda + 1|L_+|\Lambda > [S(S+1) - \Sigma(\Sigma - 1)]^{1/2},\\
&\quad \text{and}\\
&< J\Omega M| < v| < S\Sigma + 1| < \Lambda - 1|B(L_+S_-\\
&\quad +L_-S_+)|\Lambda > |S\Sigma > |v' > |J\Omega M >\\
&\quad =< v|B|v' >< \Lambda - 1|L_-|\Lambda > [S(S+1) - \Sigma(\Sigma + 1)]^{1/2}.
\end{aligned} \tag{62}
$$

(B) S-Uncoupling Interaction. H_{JS} mixes different components of the same multiplet electronic state. The selection rules are $\Delta S=0$, $\Delta\Omega=\Delta\Sigma=\pm 1$, and $\Delta\Lambda=0$. The nonzero matrix elements are

$$
\begin{aligned}
&< J\Omega \pm 1M| < v| < S\Sigma \pm 1| < \Lambda| - B(J_+S_-\\
&\quad +J_-S_+)|\Lambda > |S\Sigma > |v' > |J\Omega M >\\
&\quad = - < v|B|v' > [J(J+1) - \Omega(\Omega \pm 1)]^{1/2}\\
&\quad \times [S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}.
\end{aligned} \tag{63}
$$

(C) L-Uncoupling Interaction. If two interacting states are sufficiently far apart in energy, this L-uncoupling interaction causes the splitting between the e and f components of a degenerate Π state. This splitting is called *Λ-doubling*. If the energy interval between the two interacting states is small, this perturbation results in a large and strongly J-dependent Λ-doubling. This is responsible for the transition from Hund's case (a) to case (d). The selection rules are $\Delta S=0$, $\Delta\Omega=\Delta\Lambda=\pm 1$, and $\Delta\Sigma=0$. The nonzero matrix elements are

$$
\begin{aligned}
&< J\Omega + 1M| < v| < S\Sigma| < \Lambda + 1| - B(J_+L_-\\
&\quad +J_-L_+)|\Lambda > |S\Sigma > |v' > |J\Omega M >\\
&\quad = - < v|B|v' > [J(J+1) - \Omega(\Omega + 1)]^{1/2}\\
&\quad \times < \Lambda + 1|L_+|\Lambda >,\\
&\quad \text{and}\\
&< J\Omega - 1M| < v| < S\Sigma| < \Lambda - 1| - B(J_+L_-\\
&\quad +J_-L_+)|\Lambda > |S\Sigma > |v' > |J\Omega M >\\
&\quad = - < v|B|v' > [J(J+1) - \Omega(\Omega - 1)]^{1/2}\\
&\quad \times < \Lambda - 1|L_-|\Lambda > .
\end{aligned} \tag{64}
$$

Since $-B(J_+L_-+J_-L_+)=-B(J_+\sum_i l_{-i}+J_-\sum_i l_{+i})$, H_{JL} is a one-electron operator, and consequently in the single-configuration approximation, the configurations describing the two interacting states can differ by only

one spin–orbital.

(D) $^1\Pi$–$^1\Sigma^+$ Heterogeneous Perturbation and Λ-type Doubling in a $^1\Pi$ State. The eigenfunctions and the eigenvalues of $H = H_e + H_v + H_r + H_{so}$ for levels of the $^1\Pi$ and $^1\Sigma^+$ states are given by Eqs. 15, 16, 18, and 19. Off diagonal matrix elements, which come from the L-uncoupling interaction H_{JL}, are

$$\begin{aligned} &< {}^1\Pi \pm vJM|H_{JL}|{}^1\Sigma^+v'JM > \\ &\quad = -[J(J+1)/2]^{1/2} < v|B|v' > [< 1|L_+|0^+ > \\ &\quad \pm < -1|L_-|0^+ >]. \end{aligned} \tag{65}$$

Since $<1|L_+|0^+>=<-1|L_-|0^+>$, we have

$$\begin{aligned} &< {}^1\Pi + vJM|H_{JL}|{}^1\Sigma^+v'JM > \\ &\quad = -[2J(J+1)]^{1/2} < v|B|v' >< 1|L_+|0^+ >, \\ &< {}^1\Pi - vJM|H_{JL}|{}^1\Sigma^+v'JM >= 0. \end{aligned} \tag{66}$$

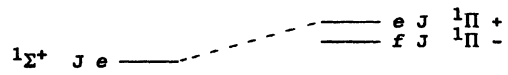
Diagonalization of the resulting 2×2 matrix between $|{}^1\Pi + vJM>$ and $|{}^1\Sigma^+v'JM>$ yields the level energies

$$\begin{aligned} E_\pm = &[E({}^1\Pi vJM) + E({}^1\Sigma^+v'JM)]/2 \\ &\pm\{[E({}^1\Pi vJM) - E({}^1\Sigma^+v'JM)]^2/4 \\ &+2J(J+1) < v|B|v' >^2 < 1|L_+|0^+ >^2\}^{1/2}. \end{aligned} \tag{67}$$

If the rotational levels of the $^1\Sigma^+$ state and the $^1\Pi$ state are separated by an energy large compared to the L-uncoupling energy, the Λ-doubled rotational levels of the $^1\Pi$ state are given by

$$\begin{aligned} &E({}^1\Pi - vJM) \\ &\quad = E({}^1\Pi v) + B_v(\Pi)[J(J+1) - 1 + < L^2 >_\Pi], \\ &E({}^1\Pi + vJM) \\ &\quad = E({}^1\Pi v) + B_v(\Pi)[J(J+1) - 1 + < L^2 >_\Pi] \\ &\quad +2J(J+1) < v|B|v' >^2 < 1|L_+|0^+ >^2 \\ &\quad /[E({}^1\Pi vJM) - E({}^1\Sigma^+v'JM)]. \end{aligned} \tag{68}$$

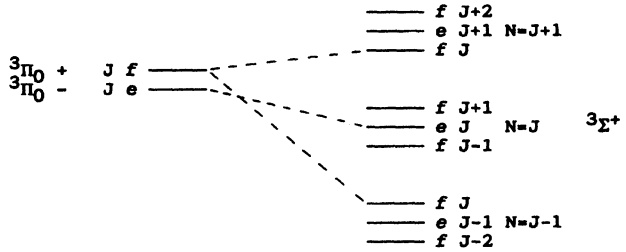
If the rotational energy levels of the $^1\Sigma^+$ state cross those of the $^1\Pi$ state for some value J_c of the rotational quantum number, then the rotational levels of one component of the $^1\Pi$ state having $J \approx J_c$ will suffer equal and opposite displacements, corresponding to what might be called the usual heterogeneous perturbation.



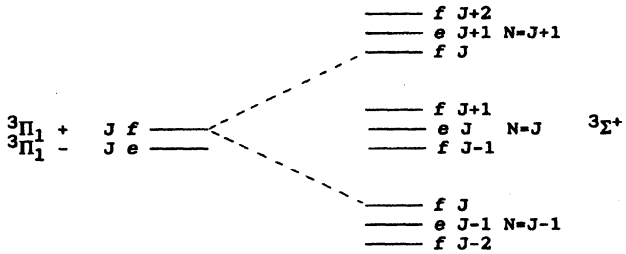
(E) $^3\Pi$–$^3\Sigma^+$ Heterogeneous Perturbation. We shall consider the $^3\Pi$–$^3\Sigma^+$ heterogeneous perturbation, which comes from the L-uncoupling interaction H_{JL}. The eigenfunctions of the $^3\Pi$ and $^3\Sigma^+$ states are given by Eqs. 21 and 24. The nonvanishing matrix elements of the L-uncoupling interaction between the $^3\Pi$ and $^3\Sigma^+$ states are

$$\begin{aligned} &< {}^3\Pi_0 + vJM|H_{JL}|{}^3\Sigma^+v'N = J+1JM > \\ &\quad = -J\left[\frac{J+1}{2J+1}\right]^{1/2} < v|B|v' >< 1|L_+|0^+ >, \\ &< {}^3\Pi_0 - vJM|H_{JL}|{}^3\Sigma^+v'N = JJM > \\ &\quad = [J(J+1)]^{1/2} < v|B|v' >< 1|L_+|0^+ >, \\ &< {}^3\Pi_0 + vJM|H_{JL}|{}^3\Sigma^+v'N = J-1JM > \\ &\quad = -(J+1)\left[\frac{J}{2J+1}\right]^{1/2} < v|B|v' >< 1|L_+|0^+ >, \end{aligned} \tag{69}$$

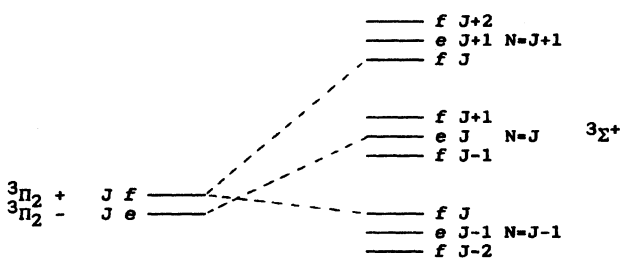
where we used the relation $<1|L_+|0^+>=<-1|L_-|0^+>$.



$$\begin{aligned} &< {}^3\Pi_1 + vJM|H_{JL}|{}^3\Sigma^+v'N = J+1JM > \\ &\quad = (J+1)\left[\frac{2J}{2J+1}\right]^{1/2} < v|B|v' >< 1|L_+|0^+ >, \\ &< {}^3\Pi_1 + vJM|H_{JL}|{}^3\Sigma^+v'N = J-1JM > \\ &\quad = -J\left[\frac{2(J+1)}{2J+1}\right]^{1/2} < v|B|v' >< 1|L_+|0^+ >, \end{aligned} \tag{70}$$



$$\begin{aligned} &< {}^3\Pi_2 + vJM|H_{JL}|{}^3\Sigma^+v'N = J+1JM > \\ &\quad = -\left[\frac{J\{J(J+1)-2\}}{2J+1}\right]^{1/2} < v|B|v' >< 1|L_+|0^+ >, \\ &< {}^3\Pi_2 - vJM|H_{JL}|{}^3\Sigma^+v'N = JJM > \\ &\quad = -[J(J+1)-2]^{1/2} < v|B|v' >< 1|L_+|0^+ >, \\ &< {}^3\Pi_2 + vJM|H_{JL}|{}^3\Sigma^+v'N = J-1JM > \\ &\quad = -\left[\frac{(J+1)\{J(J+1)-2\}}{2J+1}\right]^{1/2} \\ &\quad \times < v|B|v' >< 1|L_+|0^+ >. \end{aligned} \tag{71}$$



Hereafter, we shall consider the interactions which are not included in the Hamiltonian $H=H_e+H_v+H_r+H_{so}$.

5. Spin–Rotation Interaction and Spin–Spin Interaction

(A) Spin–Rotation Interaction. The effective Hamiltonian for the spin–rotation interaction, which is the interaction between the electron spins and the magnetic field created by nuclear motion, is given by[6]

$$\begin{aligned} H_{SR} &= \gamma(\boldsymbol{J}-\boldsymbol{L}-\boldsymbol{S})\cdot\boldsymbol{S} \\ &= \gamma[(1/2)(J_+S_- + J_-S_+) + J_zS_z \\ &\quad -(1/2)(L_+S_- + L_-S_+) - L_zS_z - \boldsymbol{S}^2]. \end{aligned} \tag{72}$$

The diagonal matrix element of H_{SR} for a basis function is

$$\begin{aligned} &< J\Omega M|<v|<S\Sigma|<\Lambda|H_{SR}|\Lambda>|S\Sigma>|v>|J\Omega M> \\ &\quad = \gamma_v[\Sigma^2 - S(S+1)]. \end{aligned} \tag{73}$$

The nonzero off-diagonal matrix elements are

$$\begin{aligned} &< J\Omega M|<v|<S\Sigma|<\Lambda|H_{SR}|\Lambda> \\ &\quad |S\Sigma\pm 1>|v>|J\Omega\pm 1M> \\ &\quad = (\gamma_v/2)[J(J+1)-\Omega(\Omega\pm 1)]^{1/2} \\ &\quad\quad \times[S(S+1)-\Sigma(\Sigma\pm 1)]^{1/2}, \\ &< J\Omega M|<v|<S\Sigma|<\Lambda|H_{SR}|\Lambda\mp 1> \\ &\quad |S\Sigma\pm 1>|v>|J\Omega M> \\ &\quad = -(\gamma_v/2)<\Lambda|L_\pm|\Lambda\mp 1> \\ &\quad\quad \times[S(S+1)-\Sigma(\Sigma\pm 1)]^{1/2}. \end{aligned} \tag{74}$$

The latter of Eq. 74 may be neglected for large J.

(B) Spin–Spin Interaction. The effective Hamiltonian for the spin–spin interaction, which is the interaction between the magnetic dipoles associated with the spins of two different electrons, is given by[6]

$$H_{SS} = (2/3)\lambda[3S_z^2 - \boldsymbol{S}^2]. \tag{75}$$

The nonzero matrix elements are

$$\begin{aligned} &< J\Omega M|<v|<S\Sigma|<\Lambda|H_{SS}|\Lambda>|S\Sigma>|v>|J\Omega M> \\ &\quad = (2/3)\lambda_v[3\Sigma^2 - S(S+1)]. \end{aligned} \tag{76}$$

(C) Spin–Rotation and Spin–Spin Interactions in $^3\Sigma^+$ State. The symmetric matrix elements of $H_{SR}+H_{SS}=H_S$ for basis set functions of a $^3\Sigma^+$ state are given by

$$\begin{aligned} &< J1M|<v|<11|<0^+|H_S|0^+> \\ &\quad |11>|v>|J1M> = -\gamma_v + (2/3)\lambda_v, \\ &< J1M|<v|<11|<0^+|H_S|0^+> \\ &\quad |10>|v>|J0M> = [J(J+1)/2]^{1/2}\gamma_v, \\ &< J1M|<v|<11|<0^+|H_S|0^+> \\ &\quad |1-1>|v>|J-1M> = 0, \\ &< J0M|<v|<10|<0^+|H_S|0^+> \\ &\quad |10>|v>|J0M> = -2\gamma_v - (4/3)\lambda_v, \\ &< J0M|<v|<10|<0^+|H_S|0^+> \\ &\quad |1-1>|v>|J-1M> = [J(J+1)/2]^{1/2}\gamma_v, \\ &< J-1M|<v|<1-1|<0^+|H_S|0^+> \\ &\quad |1-1>|v>|J-1M> = -\gamma_v + (2/3)\lambda_v. \end{aligned} \tag{77}$$

The nonvanishing matrix elements for wave functions given by Eq. 21 are

$$\begin{aligned} &< {}^3\Sigma^+vN=J+1JM|H_{SR}+H_{SS}|{}^3\Sigma^+vN=J+1JM> \\ &\quad = -(J+2)\gamma_v - \frac{J+2}{2J+1}(2/3)\lambda_v, \\ &< {}^3\Sigma^+vN=JJM|H_{SR}+H_{SS}|{}^3\Sigma^+vN=JJM> \\ &\quad = -\gamma_v + (2/3)\lambda_v, \\ &< {}^3\Sigma^+vN=J-1JM|H_{SR}+H_{SS}|{}^3\Sigma^+vN=J-1JM> \\ &\quad = (J-1)\gamma_v - \frac{J-1}{2J+1}(2/3)\lambda_v, \\ &< {}^3\Sigma^+vN=J+1JM|H_{SR}+H_{SS}|{}^3\Sigma^+vN=J-1JM> \\ &\quad = \frac{3[J(J+1)]^{1/2}}{2J+1}(2/3)\lambda_v. \end{aligned} \tag{78}$$

By diagonalyzing the 2×2 matrix

$$\begin{vmatrix} B_v(J+1)(J+2) & \frac{3[J(J+1)]^{1/2}}{2J+1}(2/3)\lambda_v \\ -(J+2)\gamma_v - \frac{J+2}{2J+1}(2/3)\lambda_v & \\ \frac{3[J(J+1)]^{1/2}}{2J+1}(2/3)\lambda_v & B_vJ(J-1)+(J-1)\gamma_v \\ & -\frac{J-1}{2J+1}(2/3)\lambda_v \end{vmatrix}, \tag{79}$$

we have the eigenvalues

$$\begin{aligned} F_3(N=J+1,J) &= B_vJ(J+1) - \gamma_v + (2/3)\lambda_v \\ &\quad +B_v - \gamma_v/2 - \lambda_v + \{(2J+1)^2(B_v-\gamma_v/2)^2 \\ &\quad -2\lambda_v(B_v-\gamma_v/2) + \lambda_v{}^2\}^{1/2}, \\ F_1(N=J-1,J) &= B_vJ(J+1) - \gamma_v + (2/3)\lambda_v \\ &\quad +B_v - \gamma_v/2 - \lambda_v - \{(2J+1)^2(B_v-\gamma_v/2)^2 \\ &\quad -2\lambda_v(B_v-\gamma_v/2) - \lambda_v{}^2\}^{1/2}. \end{aligned} \tag{80}$$

If we neglect λ_v and γ_v altogether, $F_3(N=J+1,J)=B_v(J+1)(J+2)$ and $F_1(N=J-1,J)=B_v(J-1)J$.

The three levels $|{}^3\Sigma^+vN=JJ-1M>$, $|{}^3\Sigma^+vN=JJM>$, and $|{}^3\Sigma^+vN=JJ+1M>$, which are degenerate when we neglect $H_{SR}+H_{SS}$, split into three components;

$$\begin{aligned} F_3(N=J,J-1) &= B_vN(N+1) - \gamma_v + (2/3)\lambda_v \\ &\quad -B_v(2N-1) - \gamma_v/2 - \lambda_v + \{(2N-1)^2 \\ &\quad \times(B_v-\gamma_v/2)^2 - 2\lambda_v(B_v-\gamma_v/2) + \lambda_v{}^2\}^{1/2}, \\ F_2(N=J,J) &= B_vN(N+1) - \gamma_v + (2/3)\lambda_v, \\ F_1(N=J,J+1) &= B_vN(N+1) - \gamma_v + (2/3)\lambda_v \\ &\quad +B_v(2N+3) - \gamma_v/2 - \lambda_v - \{(2N+3)^2 \\ &\quad \times(B_v-\gamma_v/2)^2 - 2\lambda_v(B_v-\gamma_v/2) + \lambda_v{}^2\}^{1/2}. \end{aligned} \tag{81}$$

6. Hyperfine Interaction

(A) Hyperfine Interaction Hamiltonian. The hyperfine interaction Hamiltonians for a diatomic molecule are given by[14—16]

$$H_{\rm hfs} = H_{\rm FC} + H_{\rm IL} + H_{\rm IS} + H_{\rm EQ}, \tag{82}$$

$$\begin{aligned} H_{\rm FC} &= \sum_{i,n}(8\pi/3)\zeta(n)\boldsymbol{I}(n)\cdot\boldsymbol{S}(i)\delta(\boldsymbol{r}_{in}),\\ H_{\rm IL} &= \sum_{i,n}\zeta(n)\boldsymbol{I}(n)\cdot\boldsymbol{L}(in)/{r_{in}}^3,\\ H_{\rm IS} &= \sum_{i,n}\zeta(n)[3(\boldsymbol{I}(n)\cdot\boldsymbol{r}_{in})(\boldsymbol{S}(i)\cdot\boldsymbol{r}_{in})\\ &\quad -(\boldsymbol{I}(n)\cdot\boldsymbol{S}(i)){r_{in}}^2]/{r_{in}}^5,\\ H_{\rm EQ} &= \sum_{i,n}eqQ[3(\boldsymbol{I}(n)\cdot\boldsymbol{L}(in))^2\\ &\quad +3(\boldsymbol{I}(n)\cdot\boldsymbol{L}(in))/2 - \boldsymbol{I}(n)^2\boldsymbol{L}(in)^2], \end{aligned} \tag{83}$$

where $\zeta(n)=gg_{I(n)}\mu_B\mu_N$. g, $g_{I(n)}$, μ_B, and μ_N are, respectively, the g value for an electron, g value for the nucleus n, Bohr magneton, and nuclear magneton. $\boldsymbol{L}(in)$ is the orbital angular momentum of electron i at nucleus n, $\boldsymbol{S}(i)$ is the spin of electron i, and r_{in} is the distance between electron i and the nucleus with nuclear spin $I(n)$. $H_{\rm FC}$ is the Fermi contact interaction, $H_{\rm IL}$ is nuclear spin–electron orbital angular momentum interaction, $H_{\rm IS}$ is the nuclear spin–electron spin dipole interaction, and $H_{\rm EQ}$ is the nuclear electric quadrupole interaction.

The theory of irreducible spherical tensors provides a powerful tool for calculating the matrix elements (See Appendix C).[14—16] The hyperfine interaction Hamiltonian can be written as

$$\begin{aligned} H_{\rm FC} &= \sum_n\sum_q(-)^q\\ &\quad\times[(8\pi/3)\zeta(n)\sum_i S(i)_{1q}\delta(r_{in})]I(n)_{1-q},\\ H_{\rm IL} &= \sum_n\sum_q(-)^q\\ &\quad\times[\zeta(n)\sum_i L(in)_{1q}/{r_{in}}^3]I(n)_{1-q},\\ H_{\rm IS} &= \sum_n\sum_q(-)^q\\ &\quad\times[-(10)^{1/2}\zeta(n)\sum_i T_{1q}(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3]I(n)_{1-q},\\ H_{\rm EQ} &= \sum_n\sum_q(-)^q\\ &\quad\times[3eqQ(n)\sum_i T_{2q}(\mathsf{L}(in),\mathsf{L}(in))]T_{2-q}(\mathsf{I}(n),\mathsf{I}(n)). \end{aligned} \tag{84}$$

For convenience, let us write the Hamiltonian for the hyperfine interaction as a sum of contributions from each nucleus n

$$H_{\rm hfs} = \sum_{n=1,2}[\mathsf{M}_1(n)\cdot\mathsf{I}_1(n) + \mathsf{V}_2(n)\cdot\mathsf{Q}_2(n)], \tag{85}$$

where the first term represents the magnetic dipole interaction ($H_{\rm FC}+H_{\rm IL}+H_{\rm IS}$), and the second term represents the nuclear electric quadrupole interaction. M_1 and I_1 are, respectively, the magnetic field tensor and the nuclear magnetic dipole tensor of rank 1. V_2 and Q_2 are, respectively, the electric field gradient tensor $3q\mathsf{T}_2(\mathsf{L}(in),\mathsf{L}(in))$ and the nuclear quadrupole tensor $eQ\mathsf{T}_2(\mathsf{I}(n),\mathsf{I}(n))$ of rank 2.

(B) Matrix Elements of Hyperfine Interaction. i) The Representation for Unequal Coupling. When two nuclei with nuclear spins $\boldsymbol{I}_1$ and $\boldsymbol{I}_2$ have different coupling energies, it is convenient to employ the coupling scheme

$$\begin{aligned} \boldsymbol{J} + \boldsymbol{I}_1 &= \boldsymbol{F}_1,\\ \boldsymbol{F}_1 + \boldsymbol{I}_2 &= \boldsymbol{F}_2, \end{aligned} \tag{86}$$

where the nuclear spins are coupled in order of decreasing coupling energy. The basis functions for this coupling scheme are denoted by

$$|\alpha J I_1 F_1 I_2 F_2 M_{F_2}>, \tag{87}$$

where α represents any additional quantum numbers necessary to specify the unperturbed rotational state.

Using (C8) and (C9), the matrix element for the magnetic dipole interaction of nucleus 1 is expressed as

$$\begin{aligned} &<\alpha J I_1 F_1 M_{F_1}|\mathsf{M}_1(1)\cdot\mathsf{I}_1(1)|\alpha' J' I_1 F_1' M_{F_1}'>\\ &\quad=\delta_{F_1F_1'}\delta_{M_{F_1}M_{F_1}'}(-)^{J'+I_1+F_1}\\ &\qquad\times\begin{Bmatrix} J & J' & 1\\ I_1 & I_1 & F_1\end{Bmatrix}[(2J+1)(2I_1+1)]^{1/2}\\ &\qquad\times<\alpha J\parallel\mathsf{M}_1(1)\parallel\alpha' J'><I_1\parallel\mathsf{I}_1(1)\parallel I_1>. \end{aligned} \tag{88}$$

For the electric quadrupole interaction of nucleus 1, we have

$$\begin{aligned} &<\alpha J I_1 F_1 M_{F_1}|\mathsf{V}_2(1)\cdot\mathsf{Q}_2(1)|\alpha' J' I_1 F_1' M_{F_1}'>\\ &\quad=\delta_{F_1F_1'}\delta_{M_{F_1}M_{F_1}'}(-)^{J'+I_1+F_1}\\ &\qquad\times\begin{Bmatrix} J & J' & 2\\ I_1 & I_1 & F_1\end{Bmatrix}[(2J+1)(2I_1+1)]^{1/2}\\ &\qquad\times<\alpha J\parallel\mathsf{V}_2(1)\parallel\alpha' J'><I_1\parallel\mathsf{Q}_2(1)\parallel I_1>. \end{aligned} \tag{89}$$

The results of Eqs. 88 and 89 are also applicable to the case where only one nucleus is present.

For the magnetic dipole interaction of nucleus 2, the nonvanishing matrix elements are

$$\begin{aligned} &<\alpha J I_1 F_1 I_2 F_2 M_{F_2}|\mathsf{M}_1(2)\cdot\mathsf{I}_1(2)|\alpha' J' I_1 F_1' I_2 F_2 M_{F_2}>\\ &\quad=(-)^{F_1'+I_2+F_2}\\ &\qquad\times\begin{Bmatrix} F_1 & F_1' & 1\\ I_2 & I_2 & F_2\end{Bmatrix}[(2F_1+1)(2I_2+1)]^{1/2}\\ &\qquad\times<\alpha J I_1 F_1\parallel\mathsf{M}_1(2)\parallel\alpha' J' I_1 F_1'><I_2\parallel\mathsf{I}_1(2)\parallel I_2>. \end{aligned} \tag{90}$$

Noting that $\mathsf{M}_1(2)$ acts only on the space of nucleus 2, we have

$$\begin{aligned} &<\alpha J I_1 F_1 I_2 F_2 M_{F_2}|\mathsf{M}_1(2)\cdot\mathsf{I}_1(2)|\alpha' J' I_1 F_1' I_2 F_2 M_{F_2}>\\ &\quad=(-)^a[(2F_1+1)(2F_1'+1)]^{1/2} \end{aligned}$$

$$\times \begin{Bmatrix} F_1 & F_1' & 1 \\ J' & J & I_1 \end{Bmatrix} \begin{Bmatrix} F_1 & F_1' & 1 \\ I_2 & I_2 & F_2 \end{Bmatrix} \times[(2J+1)(2I_2+1)]^{1/2} \times <\alpha J \parallel \mathsf{M}_1(2) \parallel \alpha' J' >< I_2 \parallel \mathsf{I}_1(2) \parallel I_2 >, \quad (91)$$

where $a=1+J+I_1+I_2+2F_1'+F_2$.

A similar procedure for the electric quadrupole interaction of nucleus 2 yields

$$< \alpha J I_1 F_1 I_2 F_2 M_{F_2} | \mathsf{V}_2(2) \cdot \mathsf{Q}_2(2) | \alpha' J' I_1 F_1' I_2 F_2 M_{F_2} > = (-)^b [(2F_1+1)(2F_1'+1)]^{1/2} \times \begin{Bmatrix} F_1 & F_1' & 2 \\ J' & J & I_1 \end{Bmatrix} \begin{Bmatrix} F_1 & F_1' & 2 \\ I_2 & I_2 & F_2 \end{Bmatrix} \times[(2J+1)(2I_2+1)]^{1/2} \times <\alpha J \parallel \mathsf{V}_2(2) \parallel \alpha' J' >< I_2 \parallel \mathsf{Q}_2(2) \parallel I_2 >, \quad (92)$$

where $b=J+I_1+I_2+2F_1'+F_2$.

ii) The Representation for Equal Coupling. When two nuclei with nuclear spins $\boldsymbol{I}_1$ and $\boldsymbol{I}_2$ have the same or nearly the same coupling energies, it is convenient to use the coupling scheme

$$\boldsymbol{I}_1 + \boldsymbol{I}_2 = \boldsymbol{I}, \qquad \boldsymbol{J} + \boldsymbol{I} = \boldsymbol{F}. \quad (93)$$

The basis function for this coupling scheme are denoted by

$$|\alpha J I_1 I_2 I F M_F > . \quad (94)$$

The nonvanishing matrix elements for the magnetic dipole interaction of the nucleus 1 can be written as

$$< \alpha J I_1 I_2 I F M_F | \mathsf{M}_1(1) \cdot \mathsf{I}_1(1) | \alpha' J' I_1 I_2 I' F M_F > = (-)^c [(2I+1)(2I'+1)]^{1/2} \times \begin{Bmatrix} J & J' & 1 \\ I' & I & F \end{Bmatrix} \begin{Bmatrix} I & I' & 1 \\ I_1 & I_1 & I_2 \end{Bmatrix} \times[(2J+1)(2I_1+1)]^{1/2} \times <\alpha J \parallel \mathsf{M}_1(1) \parallel \alpha' J' >< I_1 \parallel \mathsf{I}_1(1) \parallel I_1 >, \quad (95)$$

where $c=1+J'+I_1+I_2+I+I'+F$. While those for nucleus 2 are

$$< \alpha J I_1 I_2 I F M_F | \mathsf{M}_1(2) \cdot \mathsf{I}_1(2) | \alpha' J' I_1 I_2 I' F M_F > = (-)^d [(2I+1)(2I'+1)]^{1/2} \times \begin{Bmatrix} J & J' & 1 \\ I' & I & F \end{Bmatrix} \begin{Bmatrix} I & I' & 1 \\ I_2 & I_2 & I_1 \end{Bmatrix} \times[(2J+1)(2I_2+1)]^{1/2} \times <\alpha J \parallel \mathsf{M}_1(2) \parallel \alpha' J' >< I_2 \parallel \mathsf{I}_1(2) \parallel I_2 >, \quad (96)$$

where $d=1+J'+I_1+I_2+2I+F$. A similar procedure for the quadrupole interaction operator yields

$$< \alpha J I_1 I_2 I F M_F | \mathsf{V}_2(1) \cdot \mathsf{Q}_2(1) | \alpha' J' I_1 I_2 I' F M_F > = (-)^{c+1} [(2I+1)(2I'+1)]^{1/2} \times \begin{Bmatrix} J & J' & 2 \\ I' & I & F \end{Bmatrix} \begin{Bmatrix} I & I' & 2 \\ I_1 & I_1 & I_2 \end{Bmatrix} \times[(2J+1)(2I_1+1)]^{1/2} \times <\alpha J \parallel \mathsf{V}_2(1) \parallel \alpha' J' >< I_1 \parallel \mathsf{Q}_2(1) \parallel I_1 >, \quad (97)$$

while those for nucleus 2 are

$$< \alpha J I_1 I_2 I F M_F | \mathsf{V}_2(2) \cdot \mathsf{Q}_2(2) | \alpha' J' I_1 I_2 I' F M_F > = (-)^{d+1} [(2I+1)(2I'+1)]^{1/2} \times \begin{Bmatrix} J & J' & 2 \\ I' & I & F \end{Bmatrix} \begin{Bmatrix} I & I' & 2 \\ I_2 & I_2 & I_1 \end{Bmatrix} \times[(2J+1)(2I_2+1)]^{1/2} \times <\alpha J \parallel \mathsf{V}_2(2) \parallel \alpha' J' >< I_2 \parallel \mathsf{Q}_2(2) \parallel I_2 > . \quad (98)$$

iii) Reduced Matrix Elements. The angular momentum $\boldsymbol{J}$ is quantized along both spatial and molecular axes. We shall use the total angular momentum $\boldsymbol{F}$ and the nuclear spin $\boldsymbol{I}$ quantized to spatial axis. Hence, the components of tensor operators in Eq. 84 are those of the space-fixed coordinates. In order to calculate the matrix elements of an operator composed of the angular momenta $\boldsymbol{L}$ and $\boldsymbol{S}$, we must transform the operator into the molecule-fixed coordinates. Spherical tensors $\mathsf{T}^{\mathrm{s}}{}_j$ of rank j in the space-fixed coordinates and $\mathsf{T}^{\mathrm{m}}{}_j$ in the molecule-fixed coordinates are related by following equation:

$$T^{\mathrm{s}}{}_{jq} = \sum_{t=0,\pm1} (-)^{q-t} D^j_{-q-t} T^m{}_{jt}. \quad (99)$$

Let us evaluate the reduced matrix element of H_{FC}. H_{FC} is given by Eq. 84 and can be expressed as:

$$\begin{aligned} H_{\mathrm{FC}} &= \sum_n \sum_q (-)^q [(8\pi/3)\zeta(n) \sum_i S(i)_{1q} \delta(r_{in})] I(n)_{1-q} \\ &= \sum_n \sum_q (-)^q [(8\pi/3)\zeta(n) \sum_t (-)^{q-t} D^1_{-q-t} \\ &\quad \times \sum_i s(i)_{1t} \delta(r_{in})] I(n)_{1-q}. \end{aligned} \quad (100)$$

The reduced matrix element is calculated as follows:

$$\begin{aligned} &< \Lambda S \Sigma v J \parallel (8\pi/3)\zeta(n) \sum_i S(i)_{1q} \delta(r_{in}) \parallel \Lambda' S' \Sigma' v' J' > \\ &=< \Lambda S \Sigma v J \parallel (8\pi/3)\zeta(n) \sum_t (-)^{q-t} D^1_{-q-t} \\ &\quad \times \sum_i s(i)_{1t} \delta(r_{in}) \parallel \Lambda' S' \Sigma' v' J' > \\ &= \sum_t (-)^{-t} < J\Omega = \Lambda + \Sigma \parallel (-)^q D^1_{-q-t} \\ &\quad \parallel J'\Omega' = \Lambda' + \Sigma' >< \Lambda S \Sigma v | (8\pi/3)\zeta(n) \\ &\quad \times \sum_i s(i)_{1t} \delta(r_{in}) | \Lambda' S' \Sigma' v' > \\ &= \sum_t (-)^{-t} (-)^{J-\Omega'} (2J'+1)^{1/2} \begin{pmatrix} J & 1 & J' \\ -\Omega & t & \Omega' \end{pmatrix} \\ &\quad \times (-)^{S-\Sigma} \times (2S+1)^{1/2} \begin{pmatrix} S & 1 & S' \\ -\Sigma & t & \Sigma' \end{pmatrix} \\ &\quad \times < \Lambda S v \parallel (8\pi/3)\zeta(n) \sum_i s(i)_{1t} \delta(r_{in}) \parallel \Lambda' S' v' > \\ &= \delta_{\Sigma'\Sigma-t} \delta_{\Lambda'\Lambda} (-)^{-t+J-\Omega'+S-\Sigma} (2J'+1)^{1/2} \\ &\quad \times \begin{pmatrix} J & 1 & J' \\ -\Omega & t & \Omega' \end{pmatrix} \begin{pmatrix} S & 1 & S' \\ -\Sigma & t & \Sigma' \end{pmatrix} (2S+1)^{1/2} \\ &\quad \times < \Lambda S v \parallel (8\pi/3)\zeta(n) \sum_i s(i)_{1t} \delta(r_{in}) \parallel \Lambda' S' v' > . \end{aligned}$$

(101)

Thus, we can derive the nonvanishing reduced matrix elements of the tensor operators in Eq. 84 as

$$< \Lambda S\Sigma vJ \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel \Lambda S'(\Sigma - q)v'J' >= (-)^{J+S-\Lambda-2\Sigma} \times[(2S+1)(2J'+1)]^{1/2} \begin{pmatrix} S' & S & 1 \\ \Sigma - q & -\Sigma & q \end{pmatrix} \times \begin{pmatrix} J' & J & 1 \\ \Lambda+\Sigma-q & -\Lambda-\Sigma & q \end{pmatrix} K(n;\Lambda vS{:}\Lambda v'S'), \tag{102}$$

where

$$K(n;\Lambda vS{:}\Lambda v'S') = (8\pi/3)\zeta(n) < \Lambda vS \parallel \sum_i s(i)_1\delta(r_{in}) \parallel \Lambda v'S' > . \tag{103}$$

$$< \Lambda S\Sigma vJ \parallel \zeta(n)\sum_i \mathsf{L}(in)_1/{r_{in}}^3 \parallel (\Lambda - p)S\Sigma v'J' > = (-)^{J-\Lambda-\Sigma}(2J'+1)^{1/2} \times \begin{pmatrix} J' & J & 1 \\ \Lambda+\Sigma-p & -\Lambda-\Sigma & p \end{pmatrix} G(n;\Lambda v{:}\Lambda - pv'), \tag{104}$$

where

$$G(n;\Lambda v{:}\Lambda - pv') = \zeta(n) < \Lambda v|\sum_i l(in)_{1p}/{r_{in}}^3|\Lambda - pv' > . \tag{105}$$

$$< \Lambda S\Sigma vJ \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/{r_{in}}^3 \parallel (\Lambda - p)S'(\Sigma - q)v'J' > = (-)^{J+S-\Lambda+p+q}[(2S+1)(2J'+1)]^{1/2} \times \begin{pmatrix} 1 & 1 & 2 \\ -q & p+q & -p \end{pmatrix} \begin{pmatrix} S & 1 & S' \\ -\Sigma & q & \Sigma - q \end{pmatrix} \times \begin{pmatrix} J' & J & 1 \\ \Lambda+\Sigma-p-q & -\Lambda-\Sigma & p+q \end{pmatrix} (30)^{1/2} \times D(n;\Lambda vS{:}\Lambda - pv'S'), \tag{106}$$

where

$$D(n;\Lambda vS{:}\Lambda - pv'S') = \zeta(n) < \Lambda vS \parallel \sum_i s(i)_1 C_{2p}(in)/{r_{in}}^3 \parallel \Lambda - pv'S' > . \tag{107}$$

$$< I_n \parallel \mathsf{I}(n)_1 \parallel I_n >= [I_n(I_n+1)]^{1/2}. \tag{108}$$

$$< \Lambda S\Sigma vJ \parallel \sum_i 3q\mathsf{T}_2(\mathsf{L}(in),\mathsf{L}(in)) \parallel (\Lambda - p)S\Sigma v'J' > = (-)^{J-\Lambda-\Sigma}(2J'+1)^{1/2} \times \begin{pmatrix} J' & J & 2 \\ \Lambda+\Sigma-p & -\Lambda-\Sigma & p \end{pmatrix} E(n;\Lambda v{:}\Lambda - pv'), \tag{109}$$

where

$$E(n;\Lambda v{:}\Lambda - pv') =< \Lambda v \parallel \sum_i 3qT_{2p}(\mathsf{L}(in),\mathsf{L}(in)) \parallel \Lambda - pv' > . \tag{110}$$

$$< I_n \parallel eQ(n)\mathsf{T}_2(\mathsf{I}(n),\mathsf{I}(n)) \parallel I_n > = (eQ(n)/2)[(2I_n+3)(I_n+1)/I_n(2I_n-1)]^{1/2}, \tag{111}$$

where $eQ(n)$ is the nuclear quadrupole moment of nucleus n.

(C) Hyperfine Structure in the $^3\Sigma^+$ State. Nonvanishing reduced matrix elements of the Fermi contact interaction for eigenfunctions of Eq. 21 are

$$\begin{aligned}
&< {}^3\Sigma^+vN = JJ-1 \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Sigma^+vN = JJ-1 >= -\frac{1}{2J}Z(J-1)K,\\
&< {}^3\Sigma^+vN = JJ-1 \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Sigma^+vN = JJ >= -\frac{1}{2J}Z(J)K,\\
&< {}^3\Sigma^+vN = JJ \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Sigma^+vN = JJ-1 >= \frac{1}{2J}\left[\frac{2J-1}{2J+1}\right]^{1/2}Z(J)K,\\
&< {}^3\Sigma^+vN = JJ \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Sigma^+vN = JJ >= \frac{1}{2J(J+1)}Z(J)K,\\
&< {}^3\Sigma^+vN = JJ \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Sigma^+vN = JJ+1 >= -\frac{1}{2(J+1)}\left[\frac{2J+3}{2J+1}\right]^{1/2}Z(J)K,\\
&< {}^3\Sigma^+vN = JJ+1 \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Sigma^+vN = JJ >= \frac{1}{2(J+1)}Z(J)K,\\
&< {}^3\Sigma^+vN = JJ+1 \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Sigma^+vN = JJ+1 >= \frac{1}{2(J+1)}Z(J+1)K,
\end{aligned} \tag{112}$$

where

$$Z(J)K = [2J(J+1)]^{1/2}K(n;0v1{:}0v1). \tag{113}$$

There is no nonzero reduced matrix element for the nuclear spin–electron orbital angular momentum interaction H_{IL}.

Nonvanishing reduced matrix elements for the nuclear spin–electron spin dipole interaction are calculated from Eqs. 106, 107, and 21 as follows.

$$< {}^3\Sigma^+vN = JJ-1 \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Sigma^+vN = JJ-1 >= \frac{J+1}{J(2J-1)}Z(J-1)D,$$

$$< {}^3\Sigma^+vN = JJ-1 \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Sigma^+vN = JJ >= -\frac{J-2}{2J(2J-1)}Z(J)D,$$

$$< {}^3\Sigma^+vN = JJ \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Sigma^+vN = JJ-1 > = \frac{J-2}{2J(2J-1)}\left[\frac{2J-1}{2J+1}\right]^{1/2}Z(J)D,$$

$$< {}^3\Sigma^+vN = JJ \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Sigma^+vN = JJ >= \frac{1}{J(J+1)}Z(J)D,$$

$$< {}^3\Sigma^+vN = JJ \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Sigma^+vN = JJ+1 > = -\frac{J+3}{2(J+1)(2J+3)}\left[\frac{2J+3}{2J+1}\right]^{1/2}Z(J)D,$$

$$< {}^3\Sigma^+vN = JJ+1 \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Sigma^+vN = JJ >= \frac{J+3}{2(J+1)(2J+3)}Z(J)D,$$

$$< {}^3\Sigma^+vN = JJ+1 \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Sigma^+vN = JJ+1 >= -\frac{J}{(J+1)(2J+3)}Z(J+1)D,$$

$$< {}^3\Sigma^+vN = J-1J \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Sigma^+vN = J+1J > = \frac{3}{2(2J+1)}[J(J+1)]^{-1/2}Z(J)D, \quad (114)$$

where

$$Z(J)D = [2J(J+1)]^{1/2}D(n;0v1{:}0v1). \quad (115)$$

i) Heteronuclear Diatomic Molecule. When only nucleus 1 has a significant hyperfine interaction, the nonvanishing matrix elements of the magnetic dipole interaction, $H_{\mathrm{MD}}(1)=H_{\mathrm{FC}}(1)+H_{\mathrm{IL}}(1)+H_{\mathrm{IS}}(1)$, are calculated from Eqs. 88, 108, 112, 113, 114, and 115;

$$< {}^3\Sigma^+vN = JJ-1MI_1F_1M_{F_1}|H_{\mathrm{MD}}(1)| {}^3\Sigma^+vN = JJ-1MI_1F_1M_{F_1} > = [F_1J-1I_1]\left[-\frac{1}{2J}K(1;0v1{:}0v1) + \frac{J+1}{J(2J-1)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+vN = JJMI_1F_1M_{F_1}|H_{\mathrm{MD}}(1)| {}^3\Sigma^+vN = JJMI_1F_1M_{F_1} > = \{F_1JI_1\}\left[\frac{J+1}{2J+1}\right]^{1/2} \times \left[-\frac{1}{2J}K(1;0v1{:}0v1) - \frac{J-2}{2J(2J-1)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+vN = JJMI_1F_1M_{F_1}|H_{\mathrm{MD}}(1)| {}^3\Sigma^+vN = JJMI_1F_1M_{F_1} > = [F_1JI_1][\frac{1}{2J(J+1)}K(1;0v1{:}0v1) + \frac{1}{J(J+1)}D(1;0v1{:}0v1)],$$

$$< {}^3\Sigma^+vN = JJMI_1F_1M_{F_1}|H_{\mathrm{MD}}(1)| {}^3\Sigma^+vN = JJ+1MI_1F_1M_{F_1} > = \{F_1J+1I_1\}\left[\frac{J}{2J+1}\right]^{1/2} \times \left[-\frac{1}{2(J+1)}K(1;0v1{:}0v1) - \frac{J+3}{2(J+1)(2J+3)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+vN = JJ+1MI_1F_1M_{F_1}|H_{\mathrm{MD}}(1)| {}^3\Sigma^+vN = JJ+1MI_1F_1M_{F_1} > = [F_1J+1I_1]\left[\frac{1}{2(J+1)}K(1;0v1{:}0v1) - \frac{J}{(J+1)(2J+3)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+vN = J-1JMI_1F_1M_{F_1}|H_{\mathrm{MD}}(1)| {}^3\Sigma^+vN = J+1JMI_1F_1M_{F_1} >= [F_1JI_1] \times \left[\frac{3}{2(2J+1)}\{J(J+1)\}^{-1/2}D(1;0v1{:}0v1)\right], \quad (116)$$

where

$$[F_1JI_1] = (2)^{-1/2}[F_1(F_1+1) - J(J+1) - I_1(I_1+1)],$$

$$\{F_1JI_1\} = [(F_1+J+I_1+1)(J+I_1-F_1) \times (F_1+J-I_1)(F_1-J+I_1+1)/2]^{1/2}. \quad (117)$$

Using the Wigner–Eckart theorem, we have

$$< 0| < v| < 10|\sum_i s(i)_{1-1}\delta(r_{i1})|11 > |v > |0 > = (2)^{-1/2} < 0v1 \parallel \sum_i \mathsf{s}(i)_1\delta(r_{i1}) \parallel 0v1 > = (2)^{-1/2}K(1;0v1{:}0v1)/[(8\pi/3)\zeta(1)]. \quad (118)$$

For an approximate wave function expressed by a single configuration of Eq. 13, we have

$$< 0| < v| < 10|\sum_i s(i)_{1-1}\delta(r_{i1})|11 > |v > |0 > = (2)^{-1}[< \sigma s(i)|\delta(r_{i1})|\sigma s(i) > + < \sigma p_0(i)|\delta(r_{i1})|\sigma p_0(i) >]. \quad (119)$$

From Eqs. 118 and 119,

$$K(1;0v1{:}0v1) = (8\pi/3)\zeta(1) < 0v1 \parallel \sum_i \mathsf{s}(i)_1\delta(r_{i1}) \parallel 0v1 > = 2^{-1/2}(8\pi/3)\zeta(1)[< \sigma s(i)|\delta(r_{i1})|\sigma s(i) > + < \sigma p_0(i)|\delta(r_{i1})|\sigma p_0(i) >]. \quad (120)$$

Using the Wigner–Eckart theorem, we have

$$< 0| < v| < 10|\sum_i s(i)_{11}C_{20}(i1)/{r_{i1}}^3|1-1 > |v > |0 > = -(2)^{-1/2} < 0v1 \parallel \sum_i \mathsf{s}(i)_1C_{20}(i1)/{r_{i1}}^3 \parallel 0v1 > = -(2)^{-1/2}D(1;0v1{:}0v1)/\zeta(1). \quad (121)$$

For the approximate wave functions expressed by a single configuration of Eq. 13, we have

$$< 0| < v| < 10| \sum_i s(i)_{11} C_{20}(i1)/{r_{i1}}^3 |1-1> |v> |0> = -(2)^{-1}[< \sigma s(i)|C_{20}(i1)/{r_{i1}}^3|\sigma s(i)> + < \sigma p_0(i)|C_{20}(i1)/{r_{i1}}^3|\sigma p_0(i)>]. \quad (122)$$

From Eqs. 121 and 122,

$$D(1;0v1{:}0v1) = \zeta(1) < 0v1 \parallel \sum_i \mathbf{s}(i)_1 C_{20}(i1)/{r_{i1}}^3 \parallel 0v1> = (2)^{-1/2}\zeta(1)[< \sigma s(i)|C_{20}(i1)/{r_{i1}}^3|\sigma s(i)> + < \sigma p_0(i)|C_{20}(i1)/{r_{i1}}^3|\sigma p_0(i)>]. \quad (123)$$

When the coupling energy of nuclear spin I_1 is larger than the one of I_2, the nonvanishing matrix elements of the magnetic dipole interaction with I_1 are given by Eq. 116. Each hyperfine component, which is split by the interaction with nucleus 1, is split by the interaction with nucleus 2. The nonvanishing matrix elements of the magnetic dipole interaction with I_2 are given by

$$< {}^3\Sigma^+ vN = JJ-1MI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Sigma^+ vN = JJ-1MI_1F_1'I_2F_2M_{F_2}> = [J-1J-1I_1F_1F_1'I_2F_2]\left[-\frac{1}{2J}K(2;0v1{:}0v1) + \frac{J+1}{J(2J-1)}D(2;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = JJ-1MI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Sigma^+ vN = JJMI_1F_1'I_2F_2M_{F_2}> = [J-1JI_1F_1F_1'I_2F_2]\left[\frac{J+1}{J-1}\right]^{1/2} \times \left[-\frac{1}{2J}K(2;0v1{:}0v1) - \frac{J-2}{2J(2J-1)}D(2;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = JJMI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Sigma^+ vN = JJMI_1F_1'I_2F_2M_{F_2}> = [JJI_1F_1F_1'I_2F_2]\left[\frac{1}{2J(J+1)}K(2;0v1{:}0v1) + \frac{1}{J(J+1)}D(2;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = JJMI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Sigma^+ vN = JJ+1MI_1F_1'I_2F_2M_{F_2}> = [JJ+1I_1F_1F_1'I_2F_2]\left[\frac{2J+3}{2J+1}\right]^{1/2} \times \left[-\frac{1}{2(J+1)}K(2;0v1{:}0v1) - \frac{J+3}{2(J+1)(2J+3)}D(2;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = JJ+1MI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Sigma^+ vN = JJ+1MI_1F_1'I_2F_2M_{F_2}> = [J+1J+1I_1F_1F_1'I_2F_2]\left[\frac{1}{2(J+1)}K(2;0v1{:}0v1) - \frac{J}{(J+1)(2J+3)}D(2;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = J-1JMI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Sigma^+ vN = J+1JMI_1F_1'I_2F_2M_{F_2}> = [JJI_1F_1F_1'I_2F_2] \times \left[\frac{3}{2(2J+1)}\{J(J+1)\}^{-1/2}D(2;0v1{:}0v1)\right], \quad (124)$$

where

$$H_{MD}(2) = H_{FC}(2) + H_{IL}(2) + H_{IS}(2),$$

$$[JJ'I_1F_1F_1'I_2F_2] = (-)^{1+J+I_1+I_2+2F_1'+F_2}[(2F_1+1)(2F_1'+1)]^{1/2} \times \begin{Bmatrix} F_1 & F_1' & 1 \\ J' & J & I_1 \end{Bmatrix} \begin{Bmatrix} F_1 & F_1' & 1 \\ I_2 & I_2 & F_2 \end{Bmatrix} \times [(2J+1)(2I_2+1)I_2(I_2+1)2J(J+1)]^{1/2}. \quad (125)$$

ii) Homonuclear Diatomic Molecule. In a homonuclear diatomic molecule of $I_1 = I_2$, the total nuclear spin states of the same I can couple. The nonvanishing matrix elements of the magnetic dipole interaction are calculated from Eqs. 95, 96, 108, 112, 113, 114, and 115;

$$< {}^3\Sigma^+ vN = JJ-1MI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Sigma^+ vN = JJ-1MI_1I_1IFM_F> = [FJ-1I]\left[-\frac{1}{2J}K(1;0v1{:}0v1) + \frac{J+1}{J(2J-1)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = JJ-1MI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Sigma^+ vN = JJMI_1I_1IFM_F> = \{FJI\}\left[\frac{J+1}{2J+1}\right]^{1/2}\left[-\frac{1}{2J}K(1;0v1{:}0v1) - \frac{J-2}{2J(2J-1)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = JJMI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Sigma^+ vN = JJMI_1I_1IFM_F> = [FJI]\left[\frac{1}{2J(J+1)}K(1;0v1{:}0v1) + \frac{1}{J(J+1)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = JJMI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Sigma^+ vN = JJ+1MI_1I_1IFM_F> = \{FJ+1I\}\left[\frac{J}{2J+1}\right]^{1/2} \times \left[-\frac{1}{2(J+1)}K(1;0v1{:}0v1) - \frac{J+3}{2(J+1)(2J+3)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = JJ+1MI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Sigma^+ vN = JJ+1MI_1I_1IFM_F> = [FJ+1I]\left[\frac{1}{2(J+1)}K(1;0v1{:}0v1) - \frac{J}{(J+1)(2J+3)}D(1;0v1{:}0v1)\right],$$

$$< {}^3\Sigma^+ vN = J-1JMI_1I_1IFM_F| \sum_{n=1,2} H_{\rm MD}(n)|$$
$${}^3\Sigma^+ vN = J+1JMI_1I_1IFM_F >$$
$$= [FJI] \times \left[\frac{3}{2(2J+1)}\{J(J+1)\}^{-1/2} D(1;0v1{:}0v1)\right], \quad (126)$$

where $H_{\rm MD}(n)=H_{\rm FC}(n)+H_{\rm IL}(n)+H_{\rm IS}(n)$, $[FJI]$ and $\{FJI\}$ are defined by Eq. 117.

(D) Hyperfine Structure in the $^3\Pi$ State. Nonvanishing reduced matrix elements for the Fermi contact interaction are calculated from Eqs. 102, 103, and 24;

$$< {}^3\Pi_2 \pm vJM \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Pi_2 \pm vJM >= \frac{1}{2J(J+1)}(2)^{-1/2} \times [K(n;1v1{:}1v1)+K(n;-1v1{:}-1v1)]Z,$$
$$< {}^3\Pi_0 \pm vJM \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Pi_1 \pm vJM >= \frac{1}{8}[J(J+1)]^{-1/2} \times [K(n;1v1{:}1v1)+K(n;-1v1{:}-1v1)]Z,$$
$$< {}^3\Pi_1 \pm vJM \parallel (8\pi/3)\zeta(n)\sum_i \mathsf{S}(i)_1\delta(r_{in}) \parallel {}^3\Pi_2 \pm vJM >= \frac{[(J-1)(J+2)]^{1/2}}{8J(J+1)} \times [K(n;1v1{:}1v1)+K(n;-1v1{:}-1v1)]Z, \quad (127)$$

where $Z=[4J(J+1)]^{1/2}$.

Nonvanishing reduced matrix elements for the nuclear spin–electron orbital angular momentum interaction are calculated from Eqs. 104, 105, and 24;

$$< {}^3\Pi_1 \pm vJM \parallel \zeta(n)\sum_i \mathsf{L}(in)_1/{r_{in}}^3 \parallel {}^3\Pi_1 \pm vJM > = \frac{1}{4J(J+1)}[G(n;1v{:}1v)-G(n;-1v{:}-1v)]Z,$$
$$< {}^3\Pi_2 \pm vJM \parallel \zeta(n)\sum_i \mathsf{L}(in)_1/{r_{in}}^3 \parallel {}^3\Pi_2 \pm vJM > = \frac{1}{2J(J+1)}[G(n;1v{:}1v)-G(n;-1v{:}-1v)]Z. \quad (128)$$

Nonvanishing reduced matrix elements for the nuclear spin–electron spin dipole interaction are calculated from Eqs. 106, 107, and 24;

$$< {}^3\Pi_2 \pm vJM \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Pi_2 \pm vJM >= \frac{1}{J(J+1)}(2)^{-1/2} \times [D(n;1v1{:}1v1)+D(n;-1v1{:}-1v1)]Z,$$
$$< {}^3\Pi_0 \pm vJM \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Pi_1 \pm vJM >= \frac{1}{8}[J(J+1)]^{-1/2} \times [-\{D(n;1v1{:}1v1)+D(n;-1v1{:}-1v1)\} \pm (6)^{1/2}\{D(n;1v1{:}-1v1)+D(n;-1v1{:}1v1)\}]Z,$$
$$< {}^3\Pi_1 \pm vJM \parallel -(10)^{1/2}\zeta(n)\sum_i \mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_1)/r_{in}^3 \parallel {}^3\Pi_2 \pm vJM >= -\frac{[(J-1)(J+2)]^{1/2}}{8J(J+1)} \times [D(n;1v1{:}1v1)+D(n;-1v1{:}-1v1)]Z. \quad (129)$$

i) Heteronuclear Diatomic Molecule. When only nucleus 1 has a significant hyperfine interaction, the nonvanishing matrix elements of the magnetic dipole interaction are calculated from Eqs. 88, 108, 127, 128, and 129;

$$< {}^3\Pi_1 \pm vJMI_1F_1M_{F_1}|H_{\rm MD}(1)|{}^3\Pi_1 \pm vJMI_1F_1M_{F_1} > = [F_1JI_1]\frac{1}{4J(J+1)}G(1),$$
$$< {}^3\Pi_2 \pm vJMI_1F_1M_{F_1}|H_{\rm MD}(1)|{}^3\Pi_2 \pm vJMI_1F_1M_{F_1} > = [F_1JI_1]\left[\frac{1}{2J(J+1)}(2)^{-1/2}K(1) + \frac{1}{2J(J+1)}G(1) + \frac{1}{J(J+1)}(2)^{-1/2}D(1;11)\right],$$
$$< {}^3\Pi_0 \pm vJMI_1F_1M_{F_1}|H_{\rm MD}(1)|{}^3\Pi_1 \pm vJMI_1F_1M_{F_1} > = [F_1JI_1]\frac{1}{8}[J(J+1)]^{-1/2} \times [K(1)-D(1;11) \pm (6)^{1/2}D(1;1-1)],$$
$$< {}^3\Pi_1 \pm vJMI_1F_1M_{F_1}|H_{\rm MD}(1)|{}^3\Pi_2 \pm vJMI_1F_1M_{F_1} > = [F_1JI_1]\frac{[(J-1)(J+2)]^{1/2}}{8J(J+1)}[K(1)-D(1;11)], \quad (130)$$

where

$$[F_1JI_1] = F_1(F_1+1)-J(J+1)-I_1(I_1+1),$$
$$K(n) = K(n;1v1{:}1v1)+K(n;-1v1{:}-1v1),$$
$$G(n) = G(n;1v{:}1v)-G(n;-1v{:}-1v),$$
$$D(n;11) = D(n;1v1{:}1v1)+D(n;-1v1{:}-1v1),$$
$$D(n;1-1) = D(n;1v1{:}-1v1)+D(n;-1v1{:}1v1). \quad (131)$$

Using the Wigner–Eckart theorem, we have

$$< \pm1| < v| < 1-1|\sum_i s(i)_{1-1}\delta(r_{i1})|10 > |v> |\pm1> = 2^{-1/2} < \pm1v1 \parallel \sum_i s(i)_1\delta(r_{i1}) \parallel \pm1v1 > = 2^{-1/2}K(1;\pm1v1{:}\pm1v1)/[(8\pi/3)\zeta(1)]. \quad (132)$$

For the approximate wave functions expressed by a single configuration of Eq. 10, we have

$$< \pm1| < v| < 1-1|\sum_i s(i)_{1-1}\delta(r_{i1})|10 > |v> |\pm1> = 2^{-1}[< \sigma s(i)|\delta(r_{i1})|\sigma s(i) > + < \pi p_{\pm1}(i)|\delta(r_{i1})|\pi p_{\pm1}(i) >]. \quad (133)$$

From Eqs. 132 and 133,

$$K(1;\pm1v1{:}\pm1v1) = 2^{-1/2}(8\pi/3)\zeta(1)[< \sigma s(i)|\delta(r_{i1})|\sigma s(i) > + < \pi p_{\pm1}(i)|\delta(r_{i1})|\pi p_{\pm1}(i) >]. \quad (134)$$

In a similar way, we obtain

$$G(1;\pm 1v{:}\pm 1v) = \pm\zeta(1) < \pi p_{\pm 1}(i)|1/{r_{i1}}^3|\pi p_{\pm 1}(i) >,$$
$$D(1;\pm 1v1{:}\pm 1v1) = 2^{-1/2}\zeta(1)[< \sigma s(i)|C_{20}(i1)/{r_{i1}}^3|\sigma s(i) > + < \pi p_{\pm 1}(i)|C_{20}(i1)/{r_{i1}}^3|\pi p_{\pm 1}(i) >]. \quad (135)$$

By assuming primitive LCAO MOs: $|\sigma s>= 2^{-1/2}(|3s^1>+|3s^2>)$, $|\pi p_{\pm 1}>=2^{-1/2}(|3p^1_{\pm 1}>+|3p^2_{\pm 1}>)$, where $3s^n$ and $3p^n$ are atomic orbitals of nucleus n, and by neglecting the small term of $< 3p^2_{\pm 1}(i)|\delta(r_{i1})|3p^2_{\pm 1}(i)>$, we have

$$K(1;\pm 1v1{:}\pm 1v1) = 2^{-1/2}(4\pi/3)\zeta(1) < 3s^1(i)|\delta(r_{i1})|3s^1(i) > . \quad (136)$$

Hence,

$$[K(1;1v1{:}1v1) + K(1;-1v1{:}-1v1)] \approx 2^{-1/2}(8\pi/3)\zeta(1) < 3s^1(i)|\delta(r_{i1})|3s^1(i) > . \quad (137)$$

In a similar way, we have

$$G(1;\pm 1v{:}\pm 1v) = \pm[\zeta(1)/2] < 3p^1_{\pm 1}(i)|1/r^3_{i1}|3p^1_{\pm 1}(i) > . \quad (138)$$

Hence,

$$[G(1;1v{:}1v) - G(1;-1v{:}-1v)] \approx \zeta(1) < 3p^1_{\pm 1}(i)|1/{r_{i1}}^3|3p^1_{\pm 1}(i) > . \quad (139)$$

When the coupling energy of nuclear spin I_1 is larger than the one of I_2, the nonvanishing matrix elements of the magnetic dipole interaction with I_1 are given by Eq. 130. Each hyperfine component, which is split by the interaction with nucleus 1, is split by the interaction with nucleus 2. The nonvanishing matrix elements of the magnetic dipole interaction with I_2 are given by

$$< {}^3\Pi_1 \pm vJMI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Pi_1 \pm vJMI_1F_1'I_2F_2M_{F_2} > = [JJI_1F_1F_1'I_2F_2]\frac{1}{4J(J+1)}G(1),$$

$$< {}^3\Pi_2 \pm vJMI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Pi_2 \pm vJMI_1F_1'I_2F_2M_{F_2} > = [JJI_1F_1F_1'I_2F_2]\left[\frac{1}{2J(J+1)}(2)^{-1/2}K(1) + \frac{1}{2J(J+1)}G(1) + \frac{1}{J(J+1)}(2)^{-1/2}D(1;11)\right],$$

$$< {}^3\Pi_0 \pm vJMI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Pi_1 \pm vJMI_1F_1'I_2F_2M_{F_2} > = [JJI_1F_1F_1'I_2F_2]\frac{1}{8}[J(J+1)]^{-1/2} \times[K(1) - D(1;11) \pm (6)^{1/2}D(1;1-1)],$$

$$< {}^3\Pi_1 \pm vJMI_1F_1I_2F_2M_{F_2}|H_{MD}(2)| {}^3\Pi_2 \pm vJMI_1F_1'I_2F_2M_{F_2} > = [JJI_1F_1F_1'I_2F_2]\frac{[(J-1)(J+2)]^{1/2}}{8J(J+1)} \times[K(1) - D(1;11)], \quad (140)$$

where

$$[JJ'I_1F_1F_1'I_2F_2] = (-)^{1+J+I_1+I_2+2F_1'+F_2}[(2F_1+1)(2F_1'+1)]^{1/2} \times \begin{Bmatrix} F_1 & F_1' & 1 \\ J' & J & I_1 \end{Bmatrix} \begin{Bmatrix} F_1 & F_1' & 1 \\ I_2 & I_2 & F_2 \end{Bmatrix} \times[(2J+1)(2I_2+1)I_2(I_2+1)4J(J+1)]^{1/2}. \quad (141)$$

ii) Homonuclear Diatomic Molecule. In a homonuclear diatomic molecule of $I_1=I_2$, the total nuclear spin states of the same I can couple. The nonvanishing matrix elements of the magnetic dipole interaction are calculated from Eqs. 95, 96, 108, 127, 128, and 129;

$$< {}^3\Pi_1 \pm vJMI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Pi_1 \pm vJMI_1I_1IFM_F > = [FJI]\frac{1}{4J(J+1)}G(1),$$

$$< {}^3\Pi_2 \pm vJMI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Pi_2 \pm vJMI_1I_1IFM_F > = [FJI]\left[\frac{1}{2J(J+1)}(2)^{-1/2}K(1) + \frac{1}{2J(J+1)}G(1) + \frac{1}{J(J+1)}(2)^{-1/2}D(1;11)\right],$$

$$< {}^3\Pi_0 \pm vJMI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Pi_1 \pm vJMI_1I_1IFM_F > = [FJI]\frac{1}{8}[J(J+1)]^{-1/2} \times[K(1) - D(1;11) \pm (6)^{1/2}D(1;1-1)],$$

$$< {}^3\Pi_1 \pm vJMI_1I_1IFM_F|\sum_{n=1,2}H_{MD}(n)| {}^3\Pi_2 \pm vJMI_1I_1IFM_F > = [FJI]\frac{[(J-1)(J+2)]^{1/2}}{8J(J+1)}[K(1) - D(1;11)], \quad (142)$$

where $[FJI]$ is defined by Eq. 131.

(E) Intensity of Hyperfine Lines. The matrix element of the laboratory-fixed R_λ component of an electric dipole moment $\boldsymbol{\mu}$ between the hyperfine components is expressed using Eqs. 33 and C17 as

$$< \Lambda S\Sigma vJI_1F_1M_{F_1}|\mu_{R_\lambda}|\Lambda'S'\Sigma'v'J'I_1'F_1'M_{F_1}' > = \sum_{t=0,\pm 1}(-)^{\lambda-t}(-)^{F_1-M_{F_1}} \times \begin{pmatrix} F_1 & 1 & F_1' \\ -M_{F_1} & \lambda & M_{F_1}' \end{pmatrix}(2F_1+1)^{1/2} \times < \Lambda S\Sigma vJI_1F_1 \parallel D^1_{-\lambda-t}\mu_{r_t} \parallel \Lambda'S'\Sigma'v'J'I_1'F_1' > . \quad (143)$$

From Eqs. C10 and C18, we have

$$< \Lambda S\Sigma vJI_1F_1M_{F_1}|\mu_{R_\lambda}|\Lambda'S'\Sigma'v'J'I_1'F_1'M_{F_1}' > = \delta_{SS'}\delta_{\Sigma\Sigma'}\delta_{I_1I_1'}(-)^{I_1-M_{F_1}-\Lambda'-\Sigma'} \times[(2F_1+1)(2F_1'+1)(2J+1)(2J'+1)]^{1/2}$$

$$\times \begin{pmatrix} F_1 & 1 & F_1' \\ M_{F_1} & -\lambda & -M_{F_1}' \end{pmatrix} \begin{Bmatrix} F_1 & F_1' & 1 \\ J' & J & I_1 \end{Bmatrix} \sum_{t=0,\pm1} (-)^{-t} \times < \Lambda v|\mu_{r_t}|\Lambda' v' > \begin{pmatrix} J & J' & 1 \\ \Lambda+\Sigma & -\Lambda'-\Sigma' & -t \end{pmatrix}. \quad (144)$$

(F) Hyperfine Structure of Alkali-Metal Molecules. When a molecule has an electronic angular momentum, hence is in a state other than $^1\Sigma$, the magnetic dipole interaction is comparable with the hyperfine interaction found in atoms (10^3 MHz would be typical) and is usually much larger than the nuclear electric quadrupole interaction. Whenever there is an appreciable amount of an s atomic orbit in the wave function of an unpaired electron, the hyperfine interaction due to the Fermi contact interaction is expected to dominate.[17]

For Na_2 molecule of $I_{Na}=3/2$, the total nuclear spin quantum number can take the values $I=3, 2, 1, 0$. The nuclear spin functions are symmetric for odd I and antisymmetric for even I. Since the total wave function must be antisymmetric for nuclei of half-integral spin, the nuclear spin states of even I value are possible for the symmetric rotational levels (odd J level in a $^1\Sigma^+$ state) and those of odd I value are possible for antisymmetric rotational levels (even J level in a $^1\Sigma^+$ state). For a given J and I, F takes values of $J+1, J+I-1, \cdots, |J-I|$. In a $^1\Sigma^+$ state, the hyperfine structure of rotational lines for even J value consists of 7+3 components corresponding to $I=3$ and 1, while for odd J value it consists of 5+1 components corresponding to $I=2$ and 0.

7. Zeeman Interaction

The Hamiltonian of the Zeeman interaction is written as

$$\begin{aligned} H_Z &= -\boldsymbol{\mu}\cdot\boldsymbol{H} \\ &= -\mu_0 H_0 + \mu_{+1}H_{-1} + \mu_{-1}H_{+1}, \end{aligned} \quad (145)$$

where $\boldsymbol{\mu}$ is the magnetic moment of a molecule. $\boldsymbol{H}$ is the external magnetic field, $\mu_0=\mu_z$, $\mu_{\pm1}=\mp 2^{-1/2}(\mu_x \pm i\mu_y)$, $H_0=H_z$, and $H_{\pm1}=\mp 2^{-1/2}(H_x \pm iH_y)$. When the external magnetic field is along the Z axis, the components in the molecule-fixed coordinates can be written as $H_0=D^1_{00}H$, $H_{\pm1}=D^1_{0\pm1}H$ (see Eq. 33). The Hamiltonian H_Z is then written as

$$H_Z = -[\mu_0 D^1_{00} - \mu_{+1}D^1_{0-1} - \mu_{-1}D^1_{0+1}]H. \quad (146)$$

(A) Zeeman Effect for Molecules Having Electronic Angular Momentum. The orbital angular momentum $\boldsymbol{L}$ of electrons produces the magnetic dipole moment $\boldsymbol{\mu}_L=-\mu_B\boldsymbol{L}$, where μ_B is the Bohr magneton. The spin angular momentum $\boldsymbol{S}$ of electrons produces the magnetic dipole moment $\boldsymbol{\mu}_s=-g_e\mu_B\boldsymbol{S}$, where g_e is the g value for an electron ($g_e=2.002319$ for a free electron). The total electronic magnetic moment $\boldsymbol{\mu}_e$ is given by

$$\boldsymbol{\mu}_e = -\mu_B(\boldsymbol{L} + g_e\boldsymbol{S}). \quad (147)$$

i) $^1\Pi$ State. There is a magnetic moment of $-\mu_B\boldsymbol{L}$ associated with the orbital angular momentum of electrons, and the moment is along the internuclear axis. The Hamiltonian H_Z is written as

$$H_Z = \mu_B H L_0 D^1_{00}. \quad (148)$$

The Zeeman energies can be calculated from Eqs. 18 and 148 as

$$< {}^1\Pi \pm vJM|H_Z|{}^1\Pi \pm vJM >= \frac{M}{J(J+1)}\mu_B H. \quad (149)$$

The following matrix elements are also nonzero.

$$< {}^1\Pi \pm vJM|H_Z|{}^1\Pi \mp vJ+1M > = \frac{1}{(J+1)}\left[\frac{J(J+2)(J-M+1)(J+M+1)}{(2J+1)(2J+3)}\right]^{1/2}\mu_B H. \quad (150)$$

ii) $^3\Sigma^+$ State. There is a magnetic dipole moment of $-g_e\mu_B\boldsymbol{S}$ associated with the electron spin angular momentum, and the Zeeman interaction is described by

$$H_Z = g_e\mu_B H[S_0 D^1_{00} - S_{+1}D^1_{0-1} - S_{-1}D^1_{0+1}]. \quad (151)$$

The matrix elements of H_Z in the basis functions $|{}^3\Sigma^+ vN=JJ\pm1M>$ and $|{}^3\Sigma^+ vN=JJM>$ have nonvanishing elements only in 3×3 diagonal blocks of the same value of N;

$$\begin{aligned} &< {}^3\Sigma^+ vN=JJ+1M|H_Z|{}^3\Sigma^+ vN=JJ+1M > \\ &\quad = (g_e\mu_B H)M/(J+1), \\ &< {}^3\Sigma^+ vN=JJ+1M|H_Z|{}^3\Sigma^+ vN=JJM > \\ &\quad = (g_e\mu_B H)\left[\frac{J(J+M+1)(J-M+1)}{(J+1)^2(2J+1)}\right]^{1/2}, \\ &< {}^3\Sigma^+ vN=JJ+1M|H_Z|{}^3\Sigma^+ vN=JJ-1M > \\ &\quad = 0, \\ &< {}^3\Sigma^+ vN=JJM|H_Z|{}^3\Sigma^+ vN=JJM > \\ &\quad = (g_e\mu_B H)M/J(J+1), \\ &< {}^3\Sigma^+ vN=JJM|H_Z|{}^3\Sigma^+ vN=JJ-1M > \\ &\quad = (g_e\mu_B H)\left[\frac{(J+1)(J+M)(J-M)}{J^2(2J+1)}\right]^{1/2}, \\ &< {}^3\Sigma^+ vN=JJ-1M|H_Z|{}^3\Sigma^+ vN=JJ-1M > \\ &\quad = -(g_e\mu_B H)M/J. \end{aligned} \quad (152)$$

If we neglect the small energy due to the spin–rotation interaction and the spin–spin interaction, three levels of the eigenfunctions

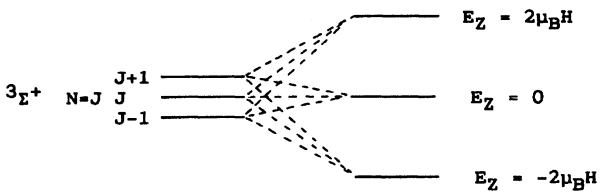
$$\begin{aligned} &|{}^3\Sigma^+ vN=JJ+1M > \\ &\quad = [(J+2)/2(2J+3)]^{1/2} \\ &\quad \times(|0^+ > |11 > |v > |J+11M > \\ &\quad +|0^+ > |1-1 > |v > |J+1-1M >) \\ &\quad +[(J+1)/(2J+3)]^{1/2}|0^+ > |10 > |v > |J+10M >, \end{aligned}$$

$$
\begin{aligned}
&|^3\Sigma^+vN = JJM> \\
&\quad = 2^{-1/2}(|0^+>|11>|v>|J1M> \\
&\quad -|0^+>|1-1>|v>|J-1M>), \\
&|^3\Sigma^+vN = JJ-1M> \\
&\quad = [(J-1)/2(2J-1)]^{1/2} \\
&\quad \times(|0^+>|11>|v>|J-11M> \\
&\quad +|0^+>|1-1>|v>|J-1-1M>) \\
&\quad -[J/(2J-1)]^{1/2}|0^+>|10>|v>|J-10M>, \quad (153)
\end{aligned}
$$

are degenerate. The eigenfunctions of a $^3\Sigma^+$ state in the presence of a magnetic field are

$$
\begin{aligned}
&|^3\Sigma^+vN = JME_Z = 2\mu_BH> \\
&\quad = \left[\frac{(J+M)(J+M+1)}{2(J+1)(2J+1)}\right]^{1/2}|^3\Sigma^+vN = JJ+1M> \\
&\quad + \left[\frac{(J+M)(J-M+1)}{2J(J+1)}\right]^{1/2}|^3\Sigma^+vN = JJM> \\
&\quad + \left[\frac{(J-M)(J-M+1)}{2J(2J+1)}\right]^{1/2}|^3\Sigma^+vN = JJ-1M>, \\
&|^3\Sigma^+vN = JME_Z = 0> \\
&\quad = -\left[\frac{(J+M+1)(J-M+1)}{(J+1)(2J+1)}\right]^{1/2} \\
&\quad \times|^3\Sigma^+vN = JJ+1M> \\
&\quad + \frac{M}{[J(J+1)]^{1/2}}|^3\Sigma^+vN = JJM> \\
&\quad + \left[\frac{(J+M)(J-M)}{J(2J+1)}\right]^{1/2}|^3\Sigma^+vN = JJ-1M>, \\
&|^3\Sigma^+vN = JME_Z = -2\mu_BH> \\
&\quad = -\left[\frac{(J-M+1)(J-M)}{2(J+1)(2J+1)}\right]^{1/2} \\
&\quad \times|^3\Sigma^+vN = JJ+1M> \\
&\quad + \left[\frac{(J-M)(J+M+1)}{2J(J+1)}\right]^{1/2}|^3\Sigma^+vN = JJM> \\
&\quad - \left[\frac{(J+M)(J+M+1)}{2J(2J+1)}\right]^{1/2}|^3\Sigma^+vN = JJ-1M>,
\end{aligned}
\quad (154)
$$

and the eigenenergies are $E_{ev}+B_vN(N+1)+2\mu_BH$, $E_{ev}+B_vN(N+1)$, and $E_{ev}+B_vN(N+1)-2\mu_BH$, respectively, where E_{ev} is the vibrational–electronic energy.



iii) $^3\Pi$ State. The Zeeman interaction is described by

$$
\begin{aligned}
H_Z &= \mu_BH[L_0D^1_{00} - L_{+1}D^1_{0-1} - L_{-1}D^1_{0+1}] \\
&\quad +g_e\mu_BH[S_0D^1_{00} - S_{+1}D^1_{0-1} - S_{-1}D^1_{0+1}]. \quad (155)
\end{aligned}
$$

The nonvanishing symmetric matrix elements for wave functions given by Eq. 24 are

$$
\begin{aligned}
&<{}^3\Pi_0 \pm vJM|H_Z|{}^3\Pi_1 \pm v'JM> \\
&\quad = g_e\mu_B<v|v'>H\frac{M}{[2J(J+1)]^{1/2}}, \\
&<{}^3\Pi_1 \pm v'JM|H_Z|{}^3\Pi_1 \pm v'JM> \\
&\quad = \mu_BH\frac{M}{J(J+1)}, \\
&<{}^3\Pi_1 \pm v'JM|H_Z|{}^3\Pi_2 \pm v''JM> \\
&\quad = g_e\mu_B<v'|v''>H\frac{M}{J(J+1)}[(J+2)(J-1)/2]^{1/2}, \\
&<{}^3\Pi_2 \pm v''JM|H_Z|{}^3\Pi_2 \pm v''JM> \\
&\quad = (1+g_e)\mu_BH\frac{2M}{J(J+1)}.
\end{aligned}
\quad (156)
$$

(B) Zeeman Structure of Hyperfine Lines. When a molecule consists of electrons with the angular momenta $\boldsymbol{L}$ and $\boldsymbol{S}$ and nuclei with the nuclear spins $\boldsymbol{I}(n)$, the magnetic moment is given by

$$
\boldsymbol{\mu} = -\mu_B(\boldsymbol{L}+g_e\boldsymbol{S}) + \sum_n g_{I(n)}\mu_N\boldsymbol{I}(n), \quad (157)
$$

where μ_N is the nuclear magneton and $g_{I(n)}$ is the nuclear g-value of nucleus n. The Zeeman Hamiltonian with an external magnetic field along the Z axis is given by the electronic and nuclear contributions;

$$
\begin{aligned}
H_Z &= H_{Ze} + H_{ZI}, \\
H_{Ze} &= -\mu_BH\sum_t(-)^tD^1_{0-t}(L_t + g_eS_t), \\
H_{ZI} &= -\mu_NH\sum_n g_{I(n)}I_0(n).
\end{aligned}
\quad (158)
$$

Notice that the $\boldsymbol{L}$ and $\boldsymbol{S}$ are operators in the molecule-fixed coordinates, and $\boldsymbol{I}$ and $\boldsymbol{F}$ are in the space-fixed coordinates. Using Eqs. C2, C10, C11, and C18, we obtain

$$
\begin{aligned}
&<\Lambda S\Sigma JI_1F_1M_{F_1}|H_{Ze}|\Lambda'S'\Sigma'J'I_1F_1'M_{F_1}'> \\
&\quad = \delta_{M_{F_1}M_{F_1}'}\sum_t(-\mu_BH)(-)^{F_1-M_{F_1}} \\
&\quad \times\begin{pmatrix} F_1 & 1 & F_1' \\ -M_{F_1} & 0 & M_{F_1} \end{pmatrix}(-)^{I_1+J+F_1'+1} \\
&\quad \times[(2F_1+1)(2F_1'+1)]^{1/2}\begin{Bmatrix} F_1 & F_1' & 1 \\ J' & J & I_1 \end{Bmatrix} \\
&\quad \times(-)^{J-\Lambda-\Sigma}\begin{pmatrix} J & 1 & J' \\ -\Lambda-\Sigma & t & \Lambda'+\Sigma' \end{pmatrix} \\
&\quad \times[(2J+1)(2J'+1)]^{1/2}(<\Lambda|L_t|\Lambda'><S\Sigma|S'\Sigma'> \\
&\quad +g_e<S\Sigma|S_t|S'\Sigma'><\Lambda|\Lambda'>),
\end{aligned}
\quad (159)
$$

$$
\begin{aligned}
&<\Lambda S\Sigma JI_1F_1M_{F_1}|H_{ZI}(1)|\Lambda'S'\Sigma'J'I_1F_1'M_{F_1}'> \\
&\quad = \delta_{\Lambda\Lambda'}\delta_{SS'}\delta_{\Sigma\Sigma'}\delta_{JJ'}\delta_{M_{F_1}M_{F_1}'}(-\mu_Ng_{I(1)}H) \\
&\quad \times(-)^{F_1-M_{F_1}}\begin{pmatrix} F_1 & 1 & F_1' \\ -M_{F_1} & 0 & M_{F_1} \end{pmatrix}(-)^{I_1+J+F_1+1} \\
&\quad \times[(2F_1+1)(2F_1'+1)]^{1/2}\begin{Bmatrix} F_1 & F_1' & 1 \\ I_1 & I_1 & J \end{Bmatrix} \\
&\quad \times[I_1(I_1+1)(2I_1+1)]^{1/2}.
\end{aligned}
\quad (160)
$$

In the weak-field case, the nuclear spin $\boldsymbol{I}$ remains coupled to $\boldsymbol{J}$, and the resultant $\boldsymbol{F}$ is a good quantum number.

In the intermediate field case (i.e. hyperfine and Zeeman energies are small compared to the rotational line spacing), $\boldsymbol{I}$ and $\boldsymbol{J}$ interact more strongly with the field than with each other. The matrix elements of H_Z off diagonal in Σ are of importance in the intermediate coupling case.

i) $^3\Sigma^+$ State of NaK. There is a magnetic dipole moment associated with the electron spin angular momentum, and the one associated with the orbital angular momentum is zero. The magnetic dipole moment due to the nuclear spin is much smaller than the one due to the electronic angular momentum, and it can be neglected. Hence the matrix element of the Zeeman interaction is given by

$$\begin{aligned}
&< 01\Sigma JI_1F_1M_{F_1}|H_Z|01\Sigma' J'I_1F_1'M_{F_1} > \\
&\quad = (-g_e\mu_B H)(-)^{F_1-M_{F_1}}\begin{pmatrix} F_1 & 1 & F_1' \\ -M_{F_1} & 0 & M_{F_1}\end{pmatrix} \\
&\quad \times(-)^{I_1+J+F_1'+1}[(2F_1+1)(2F_1'+1)]^{1/2} \\
&\quad \times\begin{Bmatrix} I_1 & J & F_1 \\ 1 & F_1' & J'\end{Bmatrix}[(2J+1)(2J'+1)]^{1/2} \\
&\quad \times\sum_t(-)^{J-\Sigma}\begin{pmatrix} J & 1 & J' \\ -\Sigma & t & \Sigma'\end{pmatrix} < 1\Sigma \parallel S_{1t} \parallel 1\Sigma' > .
\end{aligned} \tag{161}$$

The matrix elements of the Zeeman interaction between the hyperfine levels $|^3\Sigma^+ vN{=}JJ{+}1IFM_F>$, $|^3\Sigma^+ vN{=}JJIFM_F>$, and $|^3\Sigma^+ vN{=}JJ{-}1IFM_F>$, which are degenerate within the small energies of the spin–rotation interaction and the spin–spin interaction, are

$$\begin{aligned}
&< {}^3\Sigma^+ vN = JJ+1IF_1M_F|H_Z| \\
&\quad {}^3\Sigma^+ vN = JJ+1IF_1'M_F > \\
&\quad = B\begin{Bmatrix} I & J+1 & F_1 \\ 1 & F_1' & J+1\end{Bmatrix}\left[\frac{(J+2)(2J+3)}{J+1}\right]^{1/2}, \\
&< {}^3\Sigma^+ vN = JJ+1IF_1M_F|H_Z|{}^3\Sigma^+ vN = JJIF_1'M_F > \\
&\quad = B\begin{Bmatrix} I & J+1 & F_1 \\ 1 & F_1' & J\end{Bmatrix}\left[\frac{J(2J+3)}{J+1}\right]^{1/2}, \\
&< {}^3\Sigma^+ vN = JJ+1IF_1M_F|H_Z| \\
&\quad {}^3\Sigma^+ vN = JJ-1IF_1'M_F >= 0, \\
&< {}^3\Sigma^+ vN = JJIF_1M_F|H_Z|{}^3\Sigma^+ vN = JJIF_1'M_F > \\
&\quad = -B\begin{Bmatrix} I & J & F_1 \\ 1 & F_1' & J\end{Bmatrix}\left[\frac{2J+1}{J(J+1)}\right]^{1/2}, \\
&< {}^3\Sigma^+ vN = JJIF_1M_F|H_Z| \\
&\quad {}^3\Sigma^+ vN = JJ-1IF_1'M_F > \\
&\quad = -B\begin{Bmatrix} I & J & F_1 \\ 1 & F_1' & J-1\end{Bmatrix}\left[\frac{(J+1)(2J-1)}{J}\right]^{1/2}, \\
&< {}^3\Sigma^+ vN = JJ-1IF_1M_F|H_Z| \\
&\quad {}^3\Sigma^+ vN = JJ-1IF_1'M_F > \\
&\quad = -B\begin{Bmatrix} I & J-1 & F_1 \\ 1 & F_1' & J-1\end{Bmatrix}\left[\frac{(J-1)(2J-1)}{J}\right]^{1/2},
\end{aligned} \tag{162}$$

where

$$\begin{aligned}
B &= (-g_e\mu_B H)(-)^{F_1-M_F}\begin{pmatrix} F_1 & 1 & F_1' \\ -M_F & 0 & M_F\end{pmatrix} \\
&\quad \times(-)^{I+J+F_1'}[(2F_1+1)(2F_1'+1)]^{1/2}.
\end{aligned} \tag{163}$$

In the weak field, the magnitude of the Zeeman splitting can be expressed by the diagonal term in F.

$$\begin{aligned}
&< {}^3\Sigma^+ vN = JJ+1IFM_F|H_Z|{}^3\Sigma^+ vN = JJ+1IFM_F > \\
&\quad = B\begin{Bmatrix} I & J+1 & F \\ 1 & F & J+1\end{Bmatrix}\left[\frac{(J+2)(2J+3)}{J+1}\right]^{1/2}, \\
&< {}^3\Sigma^+ vN = JJIFM_F|H_Z|{}^3\Sigma^+ vN = JJIFM_F > \\
&\quad = -B\begin{Bmatrix} I & J & F \\ 1 & F & J\end{Bmatrix}\left[\frac{2J+1}{J(J+1)}\right]^{1/2}, \\
&< {}^3\Sigma^+ vN = JJ-1IFM_F|H_Z|{}^3\Sigma^+ vN = JJ-1IFM_F > \\
&\quad = -B\begin{Bmatrix} I & J-1 & F \\ 1 & F & J-1\end{Bmatrix}\left[\frac{(J-1)(2J-1)}{J}\right]^{1/2},
\end{aligned} \tag{164}$$

where

$$B = (-g_e\mu_B H)(-)^{I+J+F}M_F[(2F+1)/F(F+1)]^{1/2}. \tag{165}$$

In the intermediate field case, F is no longer a good quantum number, but N is still fairly well defined (i.e. hyperfine and Zeeman energies are small compared to spacings between N levels). When the Zeeman energy is not much smaller than the hyperfine energy, the second-order perturbation theory must be used, or a complete secular equation must be solved for larger fields. In a magnetic field strong enough to decouple $\boldsymbol{I}$ and $\boldsymbol{J}$, the Zeeman effect is just the one found when no hyperfine structure is present.[7]

ii) Zeeman Perturbation between $d^3\Pi_0$ and $c^3\Sigma^+$ States of Cs_2. We shall consider the perturbation between the $d^3\Pi_0$ and $c^3\Sigma^+$ states induced by the Zeeman interaction H_Z. The eigenfunctions of the $^3\Pi_0$ and $^3\Sigma^+$ states are given by Eqs. 24 and 21. The nonvanishing symmetric matrix elements between the $^3\Pi_0(\pm vJM)$ and $^3\Sigma^+$ levels are

$$\begin{aligned}
&< {}^3\Pi_0 + vJM|H_Z|{}^3\Sigma^+ v'N = J+1J+1M > \\
&\quad = -\left[\frac{(J+2)(J-M+1)(J+M+1)}{2(J+1)(2J+1)(2J+3)}\right]^{1/2}A, \\
&< {}^3\Pi_0 + vJM|H_Z|{}^3\Sigma^+ v'N = J+1\ J\ M > \\
&\quad = \frac{M}{[2(J+1)(2J+1)]^{1/2}}A, \\
&< {}^3\Pi_0 + vJM|H_Z|{}^3\Sigma^+ v'N = J-1\ J\ M > \\
&\quad = \frac{M}{[2J(2J+1)]^{1/2}}A, \\
&< {}^3\Pi_0 + vJM|H_Z|{}^3\Sigma^+ v'N = J-1J-1M >
\end{aligned}$$

$$= \left[\frac{(J-1)(J-M)(J+M)}{2J(2J-1)(2J+1)}\right]^{1/2} A,$$

$$< {}^3\Pi_0 - vJM|H_Z|{}^3\Sigma^+ v'N = JJ+1M > = \frac{J+2}{2J+3}\left[\frac{(J-M+1)(J+M+1)}{2(J+1)(2J+1)}\right]^{1/2} A,$$

$$< {}^3\Pi_0 - vJM|H_Z|{}^3\Sigma^+ v'N = J\,J\,M > = -\frac{M}{[2J(J+1)]^{1/2}} A,$$

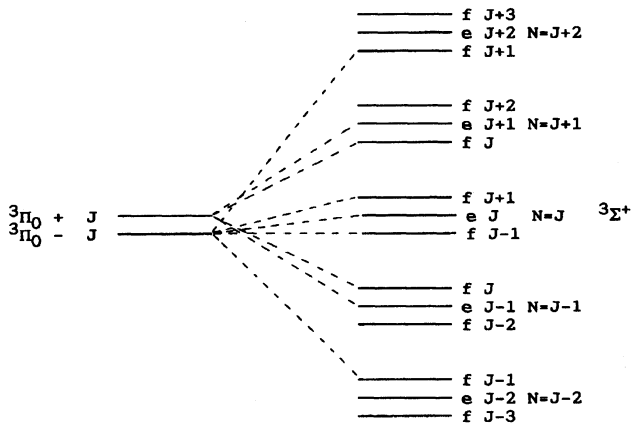
$$< {}^3\Pi_0 - vJM|H_Z|{}^3\Sigma^+ v'N = JJ-1M > = -\frac{J-1}{2J-1}\left[\frac{(J-M)(J+M)}{2J(2J+1)}\right]^{1/2} A,$$

$$< {}^3\Pi_0 - vJM|H_Z|{}^3\Sigma^+ v'N = J+2J+1M > = \frac{1}{2J+3}\left[\frac{(J+2)(J-M+1)(J+M+1)}{2(2J+1)}\right]^{1/2} A,$$

$$< {}^3\Pi_0 - vJM|H_Z|{}^3\Sigma^+ v'N = J-2J-1M > = -\frac{1}{2J-1}\left[\frac{(J-1)(J-M)(J+M)}{2(2J+1)}\right]^{1/2} A, \quad (166)$$

where

$$A = \mu_B < (\pi_u d_{+1})|(\pi_u p_{+1}) >< v|v' > H. \quad (167)$$



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Appendix A. Angular Momentum

A.1 Coupling of two Angular Momenta. We consider a system in which the total angular momentum $\boldsymbol{J}$ is the sum of $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$. If an interaction between the two parts leaves the individual angular momentum and the z-component as a constant of motion, a complete set of the eigenfunctions $|j_1 j_2 m_1 m_2>$ of H, $\boldsymbol{J}_1^2$, J_{1z}, $\boldsymbol{J}_2^2$, and J_{2z} satisfy

$$\boldsymbol{J}_1^2|j_1 j_2 m_1 m_2 >= j_1(j_1+1)|j_1 j_2 m_1 m_2 >,$$
$$J_{1z}|j_1 j_2 m_1 m_2 >= m_1|j_1 j_2 m_1 m_2 >, \quad (A1)$$

and similarly for $\boldsymbol{J}_2^2$ and J_{2z}.

A complete set of the eigenfunctions $|j_1 j_2 JM>$ of H, $\boldsymbol{J}_1^2$, $\boldsymbol{J}_2^2$, $\boldsymbol{J}^2=(\boldsymbol{J}_1+\boldsymbol{J}_2)^2$, and $J_z=J_{1z}+J_{2z}$ satisfy

$$\boldsymbol{J}^2|j_1 j_2 JM >= J(J+1)|j_1 j_2 JM >,$$
$$J_z|j_1 j_2 JM >= M|j_1 j_2 JM >, \quad (A2)$$

while $\boldsymbol{J}_1^2$ and $\boldsymbol{J}_2^2$ have the same eigenvalues as Eq. A1. The unitary transformation connecting these two representations

$$|j_1 j_2 JM > = \sum_{m_1 m_2} |j_1 j_2 m_1 m_2 >< j_1 j_2 m_1 m_2|j_1 j_2 JM >,$$
$$|j_1 j_2 m_1 m_2 > = \sum_{JM} |j_1 j_2 JM >< j_1 j_2 JM|j_1 j_2 m_1 m_2 >, \quad (A3)$$

defines the vector-addition coefficient (sometimes called a *Wigner coefficient* or *Clebsch–Gordan coefficient*). It satisfies

$$< j_1 j_2 JM|j_1 j_2 m_1 m_2 >=< j_1 j_2 m_1 m_2|j_1 j_2 JM > . \quad (A4)$$

For brevity, we shall write as:

$$< j_1 j_2 m_1 m_2|j_1 j_2 JM >=< j_1 j_2 m_1 m_2|JM >,$$
$$< j_1 j_2 JM|j_1 j_2 m_1 m_2 >=< JM|j_1 j_2 m_1 m_2 > .$$

A.2 Clebsch–Gordan Coefficients and Wigner 3-j Symbols. The *Clebsch–Gordan coefficient* (Table 2) is defined by the transformation

$$|abc\gamma >= \sum_{\alpha\beta} |ab\alpha\beta >< ab\alpha\beta|c\gamma >,$$
$$< ab\alpha\beta|c\gamma >= 0 \ \text{ unless } \ \alpha+\beta=\gamma. \quad (A5)$$

The *Wigner 3-j symbol* $\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}$ is related to *CG* coefficient by

$$< ab\alpha\beta|c-\gamma >= (-)^{a-b-\gamma}(2c+1)^{1/2}\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix},$$
$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} = 0 \ \text{ unless } \ \alpha+\beta+\gamma=0. \quad (A6)$$

Symmetry of the 3-j symbol (Table 1):

$$\begin{pmatrix} a & b & c \\ -\alpha & -\beta & -\gamma \end{pmatrix} = (-)^{a+b+c}\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}. \quad (A7)$$

Invariant under cyclic permutation of its columns:

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} = \begin{pmatrix} b & c & a \\ \beta & \gamma & \alpha \end{pmatrix}. \quad (A8)$$

Multiplied by $(-)^{a+b+c}$ upon interchange of two adjacent columns:

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} = (-)^{a+b+c}\begin{pmatrix} b & a & c \\ \beta & \alpha & \gamma \end{pmatrix}. \quad (A9)$$

A.3 Rotation matrix Elements. The rotation matrix is defined by

$$D^J_{MN} = e^{-iM\alpha} d^J_{MN}(\beta) e^{-iN\gamma}. \quad (A10)$$

Symmetry: $$(D^J_{MN})^* = (-)^{M-N} D^J_{-M-N}. \quad (A11)$$

Sum rule: $$\sum_{M'} D^J_{MM'}(D^J_{NM'})^* = \delta_{MN}. \quad (A12)$$

$$\int D^C_{cc'} D^A_{aa'} D^B_{bb'} \sin\beta \, d\beta d\alpha d\gamma = 8\pi^2 \begin{pmatrix} A & B & C \\ a & b & c \end{pmatrix}\begin{pmatrix} A & B & C \\ a' & b' & c' \end{pmatrix}. \quad (A13)$$

A.4 6-j Symbols and Racah Coefficients. 6-j symbol is defined by

$$\begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} = (-)^{a+b+c+d} W(abcd; ef), \tag{A14}$$

where $W(abcd; ef)$ is the Racah coefficient.

Symmetries: The 6-j symbol is invariant for interchange of any two columns.

$$\begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} = \begin{Bmatrix} a & e & b \\ d & f & c \end{Bmatrix} = \begin{Bmatrix} e & b & a \\ f & c & d \end{Bmatrix}, \text{ etc.} \tag{A15}$$

The 6-j symbol is invariant for interchange of the upper and lower arguments in each of any two columns.

$$\begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} = \begin{Bmatrix} a & c & f \\ d & b & e \end{Bmatrix} = \begin{Bmatrix} d & c & e \\ a & b & f \end{Bmatrix}, \text{ etc.} \tag{A16}$$

Triangular Conditions (For given j_1 and j_2, the values of J are restricted by $j_1+j_2 \geq J \geq |j_1-j_2|$): The six angular momenta in the 6-j symbol must satisfy the four triangular conditions

$$\left\{ \circ - \circ - \circ \right\}, \left\{ \circ \diagdown \circ - \circ \right\}, \left\{ \circ \diagup \circ \diagdown \circ \right\}, \left\{ \circ - \circ \diagup \circ \right\}. \tag{A17}$$

Explicit formulae

$$\begin{Bmatrix} b & b & 1 \\ c & c & a \end{Bmatrix} = \begin{Bmatrix} a & b & c \\ 1 & c & b \end{Bmatrix} = (-)^{s+1} \frac{b(b+1)+c(c+1)-a(a+1)}{[b(2b+1)(2b+2)c(2c+1)(2c+2)]^{1/2}},$$

$$\begin{Bmatrix} b & b & 1 \\ c & c-1 & a \end{Bmatrix} = \begin{Bmatrix} a & b & c \\ 1 & c-1 & b \end{Bmatrix} = (-)^{s} \left[\frac{2(s+1)(s-2a)(s-2b)(s-2c+1)}{2b(2b+1)(2b+2)(2c-1)2c(2c+1)}\right]^{1/2},$$

$$\begin{Bmatrix} b-1 & b & 1 \\ c & c-1 & a \end{Bmatrix} = \begin{Bmatrix} a & b & c \\ 1 & c-1 & b-1 \end{Bmatrix} = (-)^{s} \left[\frac{s(s+1)(s-2a-1)(s-2a)}{(2b-1)2b(2b+1)(2c-1)2c(2c+1)}\right]^{1/2},$$

$$\begin{Bmatrix} b+1 & b & 1 \\ c & c-1 & a \end{Bmatrix} = \begin{Bmatrix} a & b & c \\ 1 & c-1 & b+1 \end{Bmatrix} = (-)^{s} \times \left[\frac{(s-2b-1)(s-2b)(s-2c+1)(s-2c+2)}{(2b+1)(2b+2)(2b+3)(2c-1)2c(2c+1)}\right]^{1/2}, \tag{A18}$$

where $s=a+b+c$.

Appendix B. Transformation between the Laboratory-Fixed Coordinates and the Molecule-Fixed Coordinates

The laboratory-fixed coordinate $\boldsymbol{R}$ and the molecule-fixed coordinate $\boldsymbol{r}$ are related by

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \times \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \tilde{\mathrm{M}} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}, \tag{B1}$$

where

$$\tilde{\mathrm{M}} = \begin{pmatrix} \cos\gamma\cos\beta\cos\alpha - \sin\gamma\sin\alpha & \cos\gamma\cos\beta\sin\alpha + \sin\gamma\cos\alpha & -\cos\gamma\sin\beta \\ -\sin\gamma\cos\beta\cos\alpha - \cos\gamma\sin\alpha & -\sin\gamma\cos\beta\sin\alpha + \cos\gamma\cos\alpha & \sin\gamma\sin\beta \\ \sin\beta\cos\alpha & \sin\beta\sin\alpha & \cos\beta \end{pmatrix}. \tag{B2}$$

The Cartesian and spherical basis are related by

$$\begin{pmatrix} r_{+1} \\ r_0 \\ r_{-1} \end{pmatrix} = \tilde{\mathrm{U}} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{B3}$$

where

$$\tilde{\mathrm{U}} = \begin{pmatrix} -1/\sqrt{2} & -i/\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 1/\sqrt{2} & -i/\sqrt{2} & 0 \end{pmatrix}, \quad \tilde{\mathrm{U}}^{-1} = \begin{pmatrix} -1/\sqrt{2} & 0 & 1/\sqrt{2} \\ i/\sqrt{2} & 0 & i/\sqrt{2} \\ 0 & 1 & 0 \end{pmatrix}. \tag{B4}$$

Hence,

$$\begin{pmatrix} r_{+1} \\ r_0 \\ r_{-1} \end{pmatrix} = \tilde{\mathrm{U}} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \tilde{\mathrm{U}}\tilde{\mathrm{M}} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \tilde{\mathrm{U}}\tilde{\mathrm{M}}\tilde{\mathrm{U}}^{-1}\tilde{\mathrm{U}} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \tilde{\mathrm{U}}\tilde{\mathrm{M}}\tilde{\mathrm{U}}^{-1} \begin{pmatrix} R_{+1} \\ R_0 \\ R_{-1} \end{pmatrix}, \tag{B5}$$

$$\tilde{\mathrm{U}}\tilde{\mathrm{M}}\tilde{\mathrm{U}}^{-1} = \begin{pmatrix} e^{-i\alpha}\frac{1+\cos\beta}{2}e^{-i\gamma} & \frac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & e^{i\alpha}\frac{1-\cos\beta}{2}e^{-i\gamma} \\ -e^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} & \cos\beta & e^{i\alpha}\frac{\sin\beta}{\sqrt{2}} \\ e^{-i\alpha}\frac{1-\cos\beta}{2}e^{i\gamma} & -\frac{\sin\beta}{\sqrt{2}}e^{i\gamma} & e^{i\alpha}\frac{1+\cos\beta}{2}e^{i\gamma} \end{pmatrix}, \tag{B6}$$

$$D^1_{\lambda t} = \begin{pmatrix} e^{-i\alpha}\frac{1+\cos\beta}{2}e^{-i\gamma} & -e^{-i\alpha}\frac{\sin\beta}{\sqrt{2}} & e^{-i\alpha}\frac{1-\cos\beta}{2}e^{i\gamma} \\ \frac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & -\frac{\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\frac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\frac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\frac{1+\cos\beta}{2}e^{i\gamma} \end{pmatrix}. \tag{B7}$$

Appendix C. Tensor Operators and Their Matrix Elements

A general spherical tensor T_k of rank k is defined as a quantity represented by $2k+1$ components T_{kq} which transform according to the irreducible representation D^k of the rotation group

$$T'_{kq} = \sum_p T_{kp} D^k_{pq}(\alpha\beta\gamma). \tag{C1}$$

Wigner–Eckart Theorem. When the state vectors are eigenfunctions of $\boldsymbol{J}^2$ and J_Z, the matrix elements of a tensor operator are given by

$$< \alpha JM | T_{KQ} | \alpha' J' M' > = (-)^{J-M} \begin{pmatrix} J & K & J' \\ -M & Q & M' \end{pmatrix} (2J+1)^{1/2} \times < \alpha J \parallel \mathrm{T}_K \parallel \alpha' J' >, \tag{C2}$$

Table 1. Algebraic Formulae for the 3-j Symbols with $c=1$

$$\begin{pmatrix} J+1 & J & 1 \\ -M-1 & M & 1 \end{pmatrix} = \begin{pmatrix} J & J+1 & 1 \\ -M & M+1 & -1 \end{pmatrix} = (-)^{J-M}\left[\frac{(J+M+1)(J+M+2)}{(2J+2)(2J+1)(2J+3)}\right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ -M-1 & M & 1 \end{pmatrix} = \begin{pmatrix} J & J & 1 \\ -M & M+1 & -1 \end{pmatrix} = (-)^{J-M+1}\left[\frac{(J-M)(J+M+1)}{2J(J+1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J-1 & J & 1 \\ -M-1 & M & 1 \end{pmatrix} = \begin{pmatrix} J & J-1 & 1 \\ -M & M+1 & -1 \end{pmatrix} = (-)^{J+M}\left[\frac{(J-M-1)(J-M)}{2J(2J-1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 1 \\ -M+1 & M & -1 \end{pmatrix} = \begin{pmatrix} J & J+1 & 1 \\ -M & M-1 & 1 \end{pmatrix} = (-)^{J+M}\left[\frac{(J-M+1)(J-M+2)}{(2J+2)(2J+1)(2J+3)}\right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ -M+1 & M & -1 \end{pmatrix} = \begin{pmatrix} J & J & 1 \\ -M & M-1 & 1 \end{pmatrix} = (-)^{J+M}\left[\frac{(J+M)(J-M+1)}{2J(J+1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J-1 & J & 1 \\ -M+1 & M & -1 \end{pmatrix} = \begin{pmatrix} J & J-1 & 1 \\ -M & M-1 & 1 \end{pmatrix} = (-)^{J-M}\left[\frac{(J+M-1)(J+M)}{2J(2J-1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 1 \\ -M & M & 0 \end{pmatrix} = \begin{pmatrix} J & J+1 & 1 \\ -M & M & 0 \end{pmatrix} = (-)^{J+M+1}\left[\frac{(J-M+1)(J+M+1)}{(J+1)(2J+1)(2J+3)}\right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ -M & M & 0 \end{pmatrix} = (-)^{J+M+1}\frac{M}{[J(J+1)(2J+1)]^{1/2}}$$

$$\begin{pmatrix} J-1 & J & 1 \\ -M & M & 0 \end{pmatrix} = \begin{pmatrix} J & J-1 & 1 \\ -M & M & 0 \end{pmatrix} = (-)^{J+M}\left[\frac{(J-M)(J+M)}{J(2J-1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J & J+1 & 1 \\ -1 & 0 & 1 \end{pmatrix} = (-)^{J+1}\left[\frac{J}{2(2J+1)(2J+3)}\right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ -1 & 0 & 1 \end{pmatrix} = (-)^{J+1}\left[\frac{1}{2(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J & J-1 & 1 \\ -1 & 0 & 1 \end{pmatrix} = (-)^{J+1}\left[\frac{J+1}{2(2J-1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J & J+1 & 1 \\ 0 & -1 & 1 \end{pmatrix} = (-)^{J}\left[\frac{J+2}{2(2J+1)(2J+3)}\right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ 0 & -1 & 1 \end{pmatrix} = (-)^{J}\left[\frac{1}{2(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J & J-1 & 1 \\ 0 & -1 & 1 \end{pmatrix} = (-)^{J}\left[\frac{J-1}{2(2J-1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J & J+1 & 1 \\ 0 & 0 & 0 \end{pmatrix} = (-)^{J+1}\left[\frac{J+1}{(2J+1)(2J+3)}\right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ 0 & 0 & 0 \end{pmatrix} = 0$$

$$\begin{pmatrix} J & J-1 & 1 \\ 0 & 0 & 0 \end{pmatrix} = (-)^{J}\left[\frac{J}{(2J-1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J & J+1 & 1 \\ -1 & 1 & 0 \end{pmatrix} = (-)^{J}\left[\frac{J(J+2)}{(J+1)(2J+1)(2J+3)}\right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ -1 & 1 & 0 \end{pmatrix} = (-)^{J}\left[\frac{1}{J(J+1)(2J+1)}\right]^{1/2}$$

$$\begin{pmatrix} J & J-1 & 1 \\ -1 & 1 & 0 \end{pmatrix} = (-)^{J+1}\left[\frac{(J-1)(J+1)}{J(2J-1)(2J+1)}\right]^{1/2}$$

where $<\alpha J\|\mathsf{T}_K\|\alpha' J'>$ is independent of M and called the reduced matrix element. The reduced matrix element $(J\|\mathsf{T}_K\|J')$ defined by Edomonds[18] is related to ours by the equation

$$(J \parallel \mathsf{T}_k \parallel J') = (2J+1)^{1/2} < J \parallel \mathsf{T}_k \parallel J' > .$$

If R_{k_1} and S_{k_2} are irreducible tensors of rank k_1 and k_2 respectively, the product tensors are defined by

$$T_{KQ}(\mathsf{R}_{k_1}, \mathsf{S}_{k_2}) = (2K+1)^{1/2}(-)^{2k_2+K-Q} \times \sum_{q_1 q_2} \begin{pmatrix} K & k_1 & k_2 \\ Q & -q_1 & -q_2 \end{pmatrix} R_{k_1 q_1} S_{k_2 q_2}. \quad \text{(C3)}$$

The scalar product of two vectors of rank k is given as

$$\mathsf{R}_k \cdot \mathsf{S}_k = \sum_q (-)^q R_{kq} S_{k-q} = (-)^k (2k+1)^{1/2} T_{00}(\mathsf{R}_k, \mathsf{S}_k). \quad \text{(C4)}$$

We can derive various relations:

$$T_{00}(\mathsf{R}_1, \mathsf{S}_1) = -(\boldsymbol{R}\cdot\boldsymbol{S})/(3)^{1/2},$$
$$T_{1q}(\mathsf{R}_1, \mathsf{S}_1) = i(\boldsymbol{R}\times\boldsymbol{S})_q/(2)^{1/2}. \quad \text{(C5)}$$

If tensors S_{k_2} and O_{k_3} commute

$$\mathsf{T}_K(\mathsf{R}_{k_1}, \mathsf{S}_{k_2})\cdot\mathsf{T}_K(\mathsf{O}_{k_3}, \mathsf{P}_{k_4}) = (2K+1)(-)^{k_1+k_4} \sum_{K'} W(k_1 k_2 k_3 k_4; K K') \times \mathsf{T}_{K'}(\mathsf{R}_{k_1}, \mathsf{O}_{k_3})\cdot\mathsf{T}_{K'}(\mathsf{S}_{k_2}, \mathsf{P}_{k_4}). \quad \text{(C6)}$$

For position ($\boldsymbol{R}$) and angular momentum ($\boldsymbol{S}$ and $\boldsymbol{J}$) vectors,

$$\mathsf{T}_2(\mathsf{J}_1,\mathsf{J}_1)\cdot\mathsf{T}_2(\mathsf{J}_2,\mathsf{J}_2) = (\boldsymbol{J}_1\cdot\boldsymbol{J}_2)^2 + (1/2)(\boldsymbol{J}_1\cdot\boldsymbol{J}_2) - (1/3){J_1}^2{J_2}^2,$$

$$\mathsf{T}_2(\mathsf{S}_1,\mathsf{S}_2)\cdot\mathsf{T}_2(\mathsf{R},\mathsf{R}) = (\boldsymbol{S}_1\cdot\boldsymbol{R})(\boldsymbol{S}_2\cdot\boldsymbol{R}) - (1/3)(\boldsymbol{S}_1\cdot\boldsymbol{S}_2)R^2,$$

$$= -(10/9)^{1/2}R^2\mathsf{S}_1\cdot\mathsf{T}_1(\mathsf{C}_2,\mathsf{S}_2) = (10/3)^{1/2}\sum_{p,q}\begin{pmatrix} 1 & 1 & 2 \\ p & q-p & -q \end{pmatrix} S_{1_p}S_{2_{1q-p}}C_{2-q}. \tag{C7}$$

For the tensor operators R_k and S_k acting, respectively on subsystem 1 (characterized by the angular momentum $\boldsymbol{j}_1$) and subsystem 2 (characterized by the angular momentum $\boldsymbol{j}_2$) of a system, the matrix elements of the scalar product of these two tensor operators in the coupled basis of $\boldsymbol{J}=\boldsymbol{j}_1+\boldsymbol{j}_2$ are given by

$$\begin{aligned} &< j_1j_2JM|\mathsf{R}_k\cdot\mathsf{S}_k|j_1'j_2'J'M' > \\ &\quad = \delta_{JJ'}\delta_{MM'}(-)^k(2k+1)^{1/2} \\ &\qquad \times < j_1j_2J \parallel \mathsf{T}_0(\mathsf{R}_k,\mathsf{S}_k) \parallel j_1'j_2'J > \\ &\quad = \delta_{JJ'}\delta_{MM'} < j_1j_2J \parallel \mathsf{R}_k\cdot\mathsf{S}_k \parallel j_1'j_2'J > . \end{aligned} \tag{C8}$$

$$\begin{aligned} &< j_1j_2J \parallel \mathsf{R}_k\cdot\mathsf{S}_k \parallel j_1'j_2'J >= (-)^{j_1'+j_2+J} \\ &\qquad \times \begin{Bmatrix} j_1 & j_1' & k \\ j_2' & j_2 & J \end{Bmatrix} [(2j_1+1)(2j_2+1)]^{1/2} \\ &\qquad \times < j_1 \parallel \mathsf{R}_k \parallel j_1' >< j_2 \parallel \mathsf{S}_k \parallel j_2' >, \end{aligned} \tag{C9}$$

where the symbol in braces $\{\}$ is the 6-j symbol. For the tensor operator R_k acting only on the space of subsystem 1, the nonvanishing matrix elements are

$$\begin{aligned} &< j_1j_2J \parallel \mathsf{R}_k \parallel j_1'j_2'J' >= \delta_{j_2j_2'}(-)^{j_1+j_2+J'+k} \\ &\qquad \times[(2J'+1)(2j_1+1)]^{1/2} \begin{Bmatrix} J & J' & k \\ j_1' & j_1 & j_2 \end{Bmatrix} \\ &\qquad \times < j_1 \parallel \mathsf{R}_k \parallel j_1' > . \end{aligned} \tag{C10}$$

For the tensor operator S_k acting only on the space of subsystem 2, the nonvanishing matrix elements are

$$\begin{aligned} &< j_1j_2J \parallel \mathsf{S}_k \parallel j_1'j_2'J' >= \delta_{j_1j_1'}(-)^{j_1+j_2'+J+k} \\ &\qquad \times[(2J'+1)(2j_2+1)]^{1/2} \begin{Bmatrix} J & J' & k \\ j_2' & j_2 & j_1 \end{Bmatrix} \\ &\qquad \times < j_2 \parallel \mathsf{S}_k \parallel j_2' > . \end{aligned} \tag{C11}$$

Basic reduced matrices are;

$$\begin{aligned} &< J \parallel \mathsf{J} \parallel J' >= \delta_{JJ'}[J(J+1)]^{1/2}, \\ &< j_1j_2J \parallel \mathsf{J}_1\cdot\mathsf{J}_2 \parallel j_1'j_2'J > \\ &\quad = \delta_{j_1j_1'}\delta_{j_2j_2'}[J(J+1) - j_1(j_1+1) - j_2(j_2+1)]/2, \\ &< J \parallel \mathsf{C}_k \parallel J' >= [2J'+1]^{1/2}(-)^J \begin{pmatrix} J & k & J' \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \tag{C12}$$

The modified spherical harmonics

$$C_{jm} = [4\pi/(2j+1)]^{1/2}Y_{jm} \tag{C13}$$

is an example of spherical tensors of rank j. C_{jm} is a special case of the rotation matrix:

$$C_{jm} = {D^j_{m0}}^* = (-)^m D^j_{-m0}. \tag{C14}$$

Table 2. Clebsch–Gordan Coefficients

<1/2	1/2	0	1/2	0	1/2>	=	1,
<1/2	−1/2	0	1/2	0	−1/2>	=	1,
<1	1	1/2	1/2	1/2	1/2>	=	1,
<1	0	1/2	1/2	1/2	−1/2>	=	$1/(2)^{1/2}$,
<1	0	1/2	1/2	−1/2	1/2>	=	$1/(2)^{1/2}$,
<1	−1	1/2	1/2	−1/2	−1/2>	=	1,
<0	0	1/2	1/2	1/2	−1/2>	=	$1/(2)^{1/2}$,
<0	0	1/2	1/2	−1/2	1/2>	=	$-1/(2)^{1/2}$,
<3/2	3/2	1	1/2	1	1/2>	=	1,
<3/2	1/2	1	1/2	1	−1/2>	=	$1/(3)^{1/2}$,
<3/2	1/2	1	1/2	0	1/2>	=	$(2/3)^{1/2}$,
<3/2	−1/2	1	1/2	0	−1/2>	=	$(2/3)^{1/2}$,
<3/2	−1/2	1	1/2	−1	1/2>	=	$1/(3)^{1/2}$,
<3/2	−3/2	1	1/2	−1	−1/2>	=	1,
<1/2	1/2	1	1/2	1	−1/2>	=	$(2/3)^{1/2}$,
<1/2	1/2	1	1/2	0	1/2>	=	$-1/(3)^{1/2}$,
<1/2	−1/2	1	1/2	0	−1/2>	=	$1/(3)^{1/2}$,
<1/2	−1/2	1	1/2	−1	1/2>	=	$-(2/3)^{1/2}$,
<2	2	1/2	3/2	1/2	3/2>	=	1,
<2	1	1/2	3/2	1/2	1/2>	=	$(3/4)^{1/2}$,
<2	1	1/2	3/2	−1/2	3/2>	=	1/2,
<2	0	1/2	3/2	1/2	−1/2>	=	$1/(2)^{1/2}$,
<2	0	1/2	3/2	−1/2	1/2>	=	$1/(2)^{1/2}$,
<2	−1	1/2	3/2	1/2	−3/2>	=	1/2,
<2	−1	1/2	3/2	−1/2	−1/2>	=	$(3/4)^{1/2}$,
<2	−2	1/2	3/2	−1/2	−3/2>	=	1,
<1	1	1/2	3/2	1/2	1/2>	=	1/2,
<1	1	1/2	3/2	−1/2	3/2>	=	$-(3/4)^{1/2}$,
<1	0	1/2	3/2	1/2	−1/2>	=	$1/(2)^{1/2}$,
<1	0	1/2	3/2	−1/2	1/2>	=	$-1/(2)^{1/2}$,
<1	−1	1/2	3/2	1/2	−3/2>	=	$(3/4)^{1/2}$,
<1	−1	1/2	3/2	−1/2	−1/2>	=	−1/2.

Symmetries

$$\begin{aligned} &< JM|j_1j_2m_1m_2 >=< j_1j_2m_1m_2|JM >, \\ &< j_1j_2m_1m_2|JM > \\ &\quad = (-)^{j_1+j_2-J} < j_2j_1m_2m_1|JM >, \\ &< j_1j_2m_1m_2|JM > \\ &\quad = [(2J+1)/(2j_1+1)]^{1/2} \\ &\qquad \times(-)^{j_2+m_2} < Jj_2 - Mm_2|j_1 - m_1 > . \end{aligned}$$

Using the Wigner–Eckart theorem,

$$\begin{aligned} &< J\Omega M|C_{jm}|J'\Omega'M' > \\ &\quad =< J\Omega M|(-)^m D^j_{-m0}|J'\Omega'M' > \\ &\quad = (-)^{J-M}\begin{pmatrix} J & j & J' \\ -M & m & M' \end{pmatrix}(2J+1)^{1/2} \\ &\qquad \times < J\Omega \parallel \mathsf{C}_j \parallel J'\Omega' > . \end{aligned} \tag{C15}$$

From Eq. 3

$$|J\Omega M >= (-)^{M-\Omega}[(2J+1)/8\pi^2]^{1/2}D^J_{-M-\Omega},$$

Table 3. Matrix Elements of Rotation Matrices D^1_{pq}

$$
\begin{aligned}
&<J\ \ 0\ M|D^1_{00}|J\ \ 0\ M>=0\\
&<J\ \pm1\ M|D^1_{00}|J\ \pm1\ M>=\pm\frac{M}{J(J+1)}\\
&<J\ \pm2\ M|D^1_{00}|J\ \pm2\ M>=\pm\frac{2M}{J(J+1)}\\
&<J\ \ 0\ M|D^1_{00}|J+1\ 0\ M>=\left[\frac{(J-M+1)(J+M+1)}{(2J+1)(2J+3)}\right]^{1/2}\\
&<J\ \pm1\ M|D^1_{00}|J+1\ \pm1\ M>=\frac{1}{J+1}\left[\frac{J(J+2)(J-M+1)(J+M+1)}{(2J+1)(2J+3)}\right]^{1/2}\\
&<J\ \pm2\ M|D^1_{00}|J+1\ \pm2\ M>=\frac{1}{J+1}\left[\frac{(J-1)(J+3)(J-M+1)(J+M+1)}{(2J+1)(2J+3)}\right]^{1/2}\\
&<J\ \ 0\ M|D^1_{01}|J\ \ 1\ M>=-\frac{M}{[2J(J+1)]^{1/2}}\\
&<J\ \ 0\ M|D^1_{01}|J+1\ 1\ M>=\left[\frac{(J+2)(J-M+1)(J+M+1)}{2(J+1)(2J+1)(2J+3)}\right]^{1/2}\\
&<J\ \ 0\ M|D^1_{01}|J-1\ 1\ M>=-\left[\frac{(J-1)(J-M)(J+M)}{2J(2J-1)(2J+1)}\right]^{1/2}\\
&<J\ \ 1\ M|D^1_{01}|J\ \ 2\ M>=-\frac{M}{J(J+1)}\left[\frac{(J+2)(J-1)}{2}\right]^{1/2}\\
&<J\ \ 0\ M|D^1_{0-1}|J\ -1\ M>=\frac{M}{[2J(J+1)]^{1/2}}\\
&<J\ \ 0\ M|D^1_{0-1}|J+1\ -1\ M>=\left[\frac{(J+2)(J-M+1)(J+M+1)}{2(J+1)(2J+1)(2J+3)}\right]^{1/2}\\
&<J\ \ 0\ M|D^1_{0-1}|J-1\ -1\ M>=-\left[\frac{(J-1)(J-M)(J+M)}{2J(2J-1)(2J+1)}\right]^{1/2}\\
&<J\ -1\ M|D^1_{0-1}|J\ -2\ M>=\frac{M}{J(J+1)}\left[\frac{(J+2)(J-1)}{2}\right]^{1/2}
\end{aligned}
$$

$$< J\Omega M| = [(2J+1)/8\pi^2]^{1/2} D^J_{M\Omega}.$$

Using Eq. A13, we have (Table 3):

$$
\begin{aligned}
&< J\Omega M|D^j_{-m-q}|J'\Omega'M' >\\
&\quad = (-)^{M'-\Omega'}[(2J+1)(2J'+1)]^{1/2}\\
&\qquad \times \begin{pmatrix} J & j & J' \\ -M & m & M' \end{pmatrix}\begin{pmatrix} J & j & J' \\ -\Omega & q & \Omega' \end{pmatrix}. \qquad \text{(C16)}
\end{aligned}
$$

Similarly to Eq. C15,

$$
\begin{aligned}
&< J\Omega M|(-)^m D^j_{-m-q}|J'\Omega'M' >\\
&\quad = (-)^{J-M}\begin{pmatrix} J & j & J' \\ -M & m & M' \end{pmatrix}(2J+1)^{1/2}\\
&\qquad \times < J\Omega \parallel (-)^m D^j_{-m-q} \parallel J'\Omega' >, \qquad \text{(C17)}
\end{aligned}
$$

where

$$
\begin{aligned}
&< J\Omega \parallel (-)^m D^j_{-m-q} \parallel J'\Omega' >\\
&\quad = (-)^{J-\Omega'}(2J'+1)^{1/2}\begin{pmatrix} J & j & J' \\ -\Omega & q & \Omega' \end{pmatrix}. \qquad \text{(C18)}
\end{aligned}
$$

In the spherical basis, the vector $\boldsymbol{A}$ has the three components:

$$
\begin{aligned}
A_{+1} &= -(2)^{-1/2}(A_x + iA_y),\\
A_0 &= A_z,\\
A_{-1} &= (2)^{-1/2}(A_x - iA_y). \qquad \text{(C19)}
\end{aligned}
$$

These are the components of spherical tensor A_1 of rank 1 ($A_{1+1}\equiv A_{+1}$, $A_{10}\equiv A_0$, $A_{1-1}\equiv A_{-1}$).

$$
\begin{aligned}
\boldsymbol{A}\cdot\boldsymbol{B} &= -A_{+1}B_{-1} + A_0B_0 - A_{-1}B_{+1}\\
&= A_xB_x + A_yB_y + A_zB_z. \qquad \text{(C20)}
\end{aligned}
$$

The three components of the angular momentum $\boldsymbol{J}$ are

$$
\begin{aligned}
J_{+1} &= -(2)^{-1/2}(J_X + iJ_Y),\\
J_0 &= J_Z,\\
J_{-1} &= (2)^{-1/2}(J_X - iJ_Y). \qquad \text{(C21)}
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
&J_{+1}|JM >= -[(J-M)(J+M+1)/2]^{1/2}|JM+1>,\\
&J_0\ |JM >= M|JM>,\\
&J_{-1}|JM >= [(J+M)(J-M+1)/2]^{1/2}|JM-1>. \qquad \text{(C22)}
\end{aligned}
$$

Note that $A_{\pm1}$ defined by Eq. C19 is different from $L_\pm$, $S_\pm$, and $J_\pm$ defined in 1. (A).

$$
\begin{aligned}
&S_{+1} = -(2)^{-1/2}S_+,\\
&L_{+1} = -(2)^{-1/2}L_+,\\
&J_{+1} = -(2)^{-1/2}J_+,\\
&S_{-1} = (2)^{-1/2}S_-,\\
&L_{-1} = (2)^{-1/2}L_-,\\
&J_{-1} = (2)^{-1/2}J_-.\\
&< S\ \Sigma \pm 1|S_{\pm1}|S\Sigma >= \mp[(S\mp\Sigma)(S\pm\Sigma+1)/2]^{1/2},\\
&< L\ \Lambda \pm 1|L_{\pm1}|L\Lambda >= \mp[(L\mp\Lambda)(L\pm\Lambda+1)/2]^{1/2},\\
&< J\ \Omega \mp 1|J_{\pm1}|J\Omega >= \mp[(J\pm\Omega)(J\mp\Omega+1)/2]^{1/2},\\
&S_{+1}|1/2\ \ -1/2>= -2^{-1/2}|1/2\ \ 1/2>,\\
&S_{-1}|1/2\ \ 1/2>= 2^{-1/2}|1/2\ \ -1/2>,\\
&S_{+1}|1\ \ 0>= -|1\ \ 1>,
\end{aligned}
$$

$$S_{+1}|1\ -1>=-|1\ 0>,$$
$$S_{-1}|1\ 1>=|1\ 0>,$$
$$S_{-1}|1\ 0>=|1\ -1>. \quad \text{(C23)}$$

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