史托克及核回偶矩之合效應

Application of 3j and 6j Symbols to the Stark Effect with Hyperfine Structure

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Abstract —— The application of the Wigner-Eckart theorem and the first-order rotational representations have been used to derive the expressions of the energy matrix elements for the first and second-order perturbations and the relative intensities of the Stark effect with one nuclear quadrupole moment for the weak electric field case. The numerical values of the exact energy elements with the eigenvectors of the first-order and the second-order energy elements for $j \leq 4$ and $I \leq 3$ have been calculated. The comparsions of the relative intensities for the ammonia inversion spectrum between the previous method and the treatment presented here have been shown. The relative intensities in terms of 3j symbols for the symmetric rotors have been shown in Appendix. Some calculated values have been tabulated for illustration.

I. Introduction

The Stark effects on the rotational spectra are useful in detecting molecular absorbed lines, in identifying transitions, and in measuring dipole moments. In the Stark effect on the rotational spectra of the molecules with quadrupole nuclei, the effect of the quadrupole hyperfine structure is often large and must be taken into account. If the electric field is weak, then the interaction between the dipole moment and the electric field is considerably less than that between the nuclear quadrupole moment and the molecular electric field gradient. Therefore the Stark effect can be regarded as a perturbation upon the quadrupole hyperfine structure. Each hyperfine line is then split by the Stark effect into various components, and this splitting is small in comparsion with the hyperfine splitting. The energy levels of a rigid rotor containing at least one quadrupole nucleus and subject to a space-fixed electric field have been discussed by a number of authors [1-4]. The energy matrix elements and relative intensities described in Refs. 1 and 2 only contain the diagonal part. In fact, the off-diagonal elements are available, so that the exact energy elements should be the eigenvalues of the matrix instead of the diagonal elements. The expressions of the relative intensities shown in Refs. 2 and 3 are not adequate enough, because they do not involve the rotational and spin states which are very important in spectra. The formulas used in Ref. 4 are only for the symmetric tops. The explicit expressions of the energy elements for the second order pertubation of the asymmetric rotors have been given in Ref. 3, it is still laborious to calculate them. In order to provide the general expressions which can be used for any case and can be computed easily, this paper presents an alternate treatment, applying the Wigner-Eckart theorem and first-order rotational representations, to derive the energy matrix elements and relative intensities of the Stark effect with hyperfine structure for the weak electric field case. The forms for matrix elements and relative intensities are in terms of 3j and 6j symbols. The formulas provided in this paper can be used for the symmetric and asymmetric rotors. The energy matrix elements of the first and second-order perturbations are involved. The relative intensities contain the sufficient quantum numbers J, K, I, F, and M_F. Besides, it is easy to decide the selection rules due to the symmetry property of 3j symbols. For magnitudes, it is convenient to use either the available tables [5], or the suitable digital computer programs [6] with high-speed computers to calculate them. For being useful and convenient to the researchers interested in, the numerical values of the exact energy elements with line strengths for $J \leq 4$ and $I \leq 3$ of the symmetric tops and the energy elements of the second-order perturbation for the symmetric and

asymmetric rotors have been calculated for request.

II. Formulation

1. Energy Matrix Elements and Relative Intensities for Symmetric Tops

We consider one nucleus with a quadrupole moment. When the electric-field is weak, the rotational state J must be treated as strongly coupled to the nuclear spin state I. Then the molecular rotation precesses about the total angular momentum represented by $F = J+I$, and J, K, I, F, and M_F are good quantum numbers. Here J and K stand for the rotational energy level and M_F are projection quantum numbers of F. The interaction Hamiltonian is $-\bar{\mu} \cdot \bar{E}$. The symbols $\bar{\mu}$ and $\bar{E}$ respectively stand for the dipole moment directed along the symmetry z-axis of the symmetric top and the external electric field directed along the space-fixed Z axis. This interaction may be written as $-\mu_Z E$, here μ_Z represents the dipole moment component directed along the space-fixed Z axis. The expressions μ_Z and $\mu_0^{(1)}$ are equivalent to each other, the latter represents the spherical form. Then the energy matrix elements of the interaction Hamiltonian are

$$< J'K'IF'M_{F'}| - \mu_0^{(1)} E \mid JKIFM_F>.$$

Using the Wigner-Eckart theorem[7]

$$< \alpha'J'M'|T_q^{(k)} \mid \alpha JM > = (-1)^{J'-M'} \begin{pmatrix} J' & k & J \\ -M' & q & M \end{pmatrix}$$

$$x < \alpha'J'\|T^{(k)} \| \alpha J >, \tag{1}$$

we may express the matrix elements as

$$<J'K'IF'M_F'| \quad \mu_0^{(1)} E \mid JKIFM_F > = (-1)^{F'-M_F+1}$$

$$x \begin{pmatrix} F' & 1 & F \\ -M_F' & 0 & M_F \end{pmatrix} < J'K'IF' \| \mu^{(1)} \| JKIF > E. \tag{2}$$

By the use of the Wigner-Eckart theorem for the coupled scheme [8]

$$<\alpha'J_1'J_2J'\| T^{(k)} \| \alpha J_1 J_2 J > = (-1)^{J_1'+J_2+J+k}$$

$$x \; [(2J+1)(2J'+1)]^{\frac{1}{2}} \begin{Bmatrix} J_1' & J' & J_2 \\ J & J_1 & k \end{Bmatrix} < \alpha' J_1' \| T^{(k)} \| \alpha J_1 >, \tag{3}$$

the reduced matrix element in Eq. (2) can be further reduced to

$$< J'K'IF \| \mu^{(1)} \| JKIF > = (-1)^{J'+I+F+1}$$

$$x \; [(2F+1)(2F'+1)]^{\frac{1}{2}} \begin{Bmatrix} J' & F' & 1 \\ F & J & 1 \end{Bmatrix} <J'K'\|\mu^{(1)}\|JK> \; , \tag{4}$$

where the reduced matrix element represents the dipole moment matrix element for the symmetric top. Its explicit form in terms of 3j symbols has been shown in Eq. (A6) in Appendix, and the square of it indicates the relative intensity of a transition line. By combining Eqs. (A6), (2), and (4), we obtain the expression

$$<J'K'IF'M_F'|-\mu_o^{(1)}E|JKIFM_F> = (-1)^t \; \mu E$$

$$x \; [(2F+1)(2F'+1)]^{\frac{1}{2}} \; [(2J+1)(2J'+1)]^{\frac{1}{2}} \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix} \begin{pmatrix} F' & 1 & F \\ -M_F' & 0 & M_F \end{pmatrix}$$

$$x \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix} , \tag{5}$$

where $t = J + J' + F' + F + I - M_F - K + 1$.

The square of the dipole moment matrix elements between two states $|J'K'IF'M_F'>$ and $|JKIFM_F>$ is defined as the relative intensity. The matrix elements are

$$C = <J'K'IF'M_F'|\mu_o^{(1)}|JKIFM_F> = (-1)^{t'} \; \mu \; [(2F+1)(2F+1)]^{\frac{1}{2}}$$

$$x \; [(2J'+1)(2J+1)]^{\frac{1}{2}} \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix} \begin{pmatrix} F' & 1 & F \\ -M_F' & 0 & M_F \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix} , \tag{6}$$

where $t' = J + J' + F' + F + I - M_F - K$; the relative intensities will be

$$S(J'K'IF'M_F' \to JKIFM_F) = \left[\mu^2 (2J'+1)(2J+1) \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix}^2 \right]$$

$$x \; (2F'+1)(2F+1) \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix}^2 \begin{pmatrix} F' & 1 & F \\ -M_F' & 0 & M_F \end{pmatrix}^2 , \tag{7}$$

where the expression in the bracket represents the relative intensity of a pure rotational transition line as shown in Eq. (A7). For the identification of the Stark effect, the line strength for each component can be simply given as

$$S(J'K'IF'M_F' \to JKIFM_F) = (2F'+1)(2F+1) \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix}^2$$

$$x \begin{pmatrix} F' & 1 & F \\ -M_F' & 0 & M_F \end{pmatrix}^2 \tag{8}$$

For non-vanishing elements in Eq. (8), we find that the selection rules are $\Delta F=0$, ± 1, and $\Delta M_F=0$. Equation (8) contains, in addition to F and M_F as shown in Ref. 2, the rotational states J' and J and nuclear state I. So that it seems to be more physically adequate. In accordance with the first-order perturbation, the energy matrix elements between the states of different J will be neglected. By using Eq. (5), we can construct the energy matrix elements for a particular J, K and M_F. It should be noted that M_F can be obtained with more than one value of F. The matrix for each M_F must be diagonalized to obtain the exact energy elements. The exact energy levels, the multiplications of the exact energy elements and μE, must be added to the rotational energy for that J and K. The calculation of line strength of each component for a given rotational transition should then be modified as

$$S'(J'KIF'M_{F}' \rightarrow JKIFM_{F})$$

$$= \sum_{F_L} \sum_{F_U} \; | \, C_L \, (F_L) \, C_U(F_U) \; C \, |^2 \, , \tag{9}$$

where $C_L \, (F_L)$ and $C_U \, (F_U)$ respectively represent the eigenvectors, obtained from the diagonalizing transformation, for the lower and upper energy states, and C is defined as in Eq. (6). In fact, the pure rotational relative intensity containing in the explicit form of Eq. (9) may be omitted for a given rotational line.

If the first-order correction is not adequately good enough, the second-order perturbation will be needed. According to the second-order perturbation theory, the energy elements are given as

$$E_{JKIFM_F}^{(2)} = \sum_{J'F'} \frac{|< JKIFM_F \, | \; - \mu_o^{(1)} \, E \, |\, J'K' IF'M_{F'} >|^2}{E_{JKIF} \, - \, E_{J'K'IF'}} \, ,$$

where E_{JKIF} represents the quadrupole hyperfine energy levels which have previously been discussed in terms of the irreducible tensor operators [9, 10] . By using Eq. (5), we may rewrite the above equation as

$$E_{JKIFM_F}^{(2)} = \mu^2 E^2$$

$$\times \sum_{J'F'} \frac{[(2J'+1)\,(2J+1)] \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix}^2 [(2F'+1)\,(2F+1)] \begin{pmatrix} F' & 1 & F \\ -M_{F'} & 0 & M_F \end{pmatrix}^2 \begin{Bmatrix} J' & F' & 1 \\ F & J & I \end{Bmatrix}^2}{E_{JKIF} - E_{J'K'IF'}} \tag{10}$$

2. Energy Matrix Elements and Relative Intensities for Asymmetric Rotors

Here we consider one nuclear quadrupole moment. For this kind of rotor, the expressions J, τ, I, F, and M_F are good quantum numbers, where J and τ stand for the rotational state. By considering the Four-Group [11], we find that there are not any diagonal matrix elements for the first-order perturbation. For the second-order perturbation, the correction energy elements due to the body-fixed g axis are

$$(E_g^{(2)})_{J\tau IFM_F} = \sum_{J'\tau'F'} \frac{| < J\tau IFM_F \, |(-\mu_o^{(1)} \, E)_g \, |\, J'\tau'IF'M_{F'}>|^2}{E_{J\tau IF} - E_{J'\tau'IF'}} \, , \tag{11}$$

where the term $(\mu_o^{(1)} E)_g$ indicates the interaction between the external electric field directed along the space-fixed z axis and the dipole moment directed along the body-fixed g axis, and $E_{J\tau IF}$ represents the quadrupole hyperfine

energy. The theoretical and experimental works for hyperfine structure of the asymmetric rotors have been thoroughly discussed in terms of the irreducible tensor operators [12-17].

By the use of Eqs. (1) and (3), the matrix elements of the numerator in Eq. (11) can be expressed in the form

$$| < J\tau IFM_F \ | \ (- \mu_0^{(1)}E)_g \ | \ J'\tau'IF'M_F' > |^2 = E^2 \ (2F'+1) \ (2F+1)$$

$$x \ \begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix}^2 \ \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F' \end{pmatrix}^2 \ | < J\tau \ || \ \mu^{(1)} \ || \ J'\tau' >_g |^2 , \qquad (12)$$

where the expression $| <J \ ||\mu^{(1)} \ || \ J'\tau >_g |^2$ is the relative intensity due to the dipole moment component μ_g directed along the body-fixed g axis. The substitution of Eq. (12) into Eq. (11) gives the energy matrix elements as

$$(E_g^{(2)})_{J\tau FM_F} = \mu_g^2 \ \lambda_g E^2 \ \underset{J'\tau'F'}{\Sigma} \ \frac{(2F'+1)(2F+1) \begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix}^2 \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F' \end{pmatrix}^2}{E_{J\tau IF} - E_{J'\tau'IF'}} ,$$

where λ_g represents the line strength and $\mu_g^2 \lambda_g$ is equivalent to the relative intensity $< J\tau \ ||\mu^{(1)} \ || \ J'\tau'>_g |^2$. The procedure to calculate the magnitudes of λ_g have been presented [18], an alternate method in terms of 3j symbols will be given in another paper. The total interaction energy of the state $| J\tau IFM_F >$ will be the summation of Eq. (13) over g, it is

$$E_{J\tau IFM_F}^{(2)} = \underset{g}{\Sigma} \ E^2 \ \mu_g^2 \ \lambda_g$$

$$x \ \underset{J'\tau'F'}{\Sigma} \ \frac{(2F'+1) \ (2F+1) \begin{Bmatrix} J & F & I \\ F' & J' & 1 \end{Bmatrix}^2 \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F' \end{pmatrix}^2}{E_{J\tau IF} - E_{J'\tau'IF'}} \qquad (14)$$

The relative intensity defined as the square of the dipole moment matrix element between the two states $J'\tau'IF'M_F'>$ and $| J\tau IFM_F >$ is

$$S (J'\tau'IF'M_F' \rightarrow J\tau IFM_F)$$

$$= | < J'\tau'IF'M_F' \ | \ \mu_0^{(1)} \ | \ J\tau IFM_F >_g |^2$$

Using Eqs. (1) and (3), we have the relative intensity

$$S (J'\tau'IF'M_F' \rightarrow J\tau IFM_F) = | < J'\tau' \ ||\mu^{(1)} \ || \ J\tau >_g |^2$$

$$x \ (2F+1) \ (2F'+1) \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix}^2 \begin{pmatrix} F' & 1 & F \\ -M_F' & 0 & M_F \end{pmatrix}^2$$

The line strength of the Stark effect component for a given rotational transition can be reduced to

$$S(J' \tau' IF\ M_F' \to J\tau IFM_F) = (2F'+1)\ (2F+1)$$

$$\times \left\{ \begin{matrix} J' & F' & I \\ F & J & 1 \end{matrix} \right\}^2 \left(\begin{matrix} F' & 1 & F \\ -M_F' & 0 & M_F \end{matrix} \right)^2 \tag{15}$$

The selection rules are $\Delta F = 0,\ \pm 1$, and $\Delta M_F = 0$.

III. Results and Discussions

1. Energy Matrix Elements

The energy matrix elements of the symmetric tops have been established by Eq. (5) and diagonalized to obtain the exact energy elements and eigenvectors for the first-order perturbation. The numerical values, calculated for the quantum numbers J=4, K=3 and I=1.0 are given in Table 1. The first column represents the exact energy elements, the second one represents the eigenvectors associating with the biggest value of F, the third represents the eigenvectors associating with the smaller one by step 1, and so on. For example, when $M_F=2$, the state function for the exact energy element -0.15 will be that $|J=4, K=3, I=1; MF=2 > =0.683130\ |43152 > -0.670820\ |43142 > +0.288675\ |43132 >$. From the symmetry property of 3j symbols, we found that when J, I, and M_F are fixed, the phases of matrix elements are not affected by K, but the magnitudes are. That is the energy matrix elements for a certain value of K are K times of those for K equal to 1. So that the exact energy elements for the former are K times of those for the latter, but the eigenvectors for both cases are same. If the value of K shown in example is changed to 1, the exact energy element is that -0.05, but the eigenvectors are still same.

2. Line Strengths

The line strengths for J=3 and I=1 of the symmetric tops obtained by Eq.(9) have been calculated and given in Table 2. The first two columns represent the rotational quantum numbers and sub-quantum numbers of F for the lower energy levels, and the second two columns represent those for the upper energy levels. The fifth one represents the exact line strengths. The sixth and seventh ones represent the exact energy elements respectively for the lower and upper rotational energy levels. And the last one represents the difference between two rotational states. It was found that the sub-quantum number K containing in the power in Eq. (6) does not affect the magnitudes of line strengths, since it is not involved 3j and 6j symbols. The magnitudes of the exact energy elements given in Table 2 are only for K=1, but the line strengths can be used for any allowed values of K.

3. Second-Order Perturbation Energy Elements

Table 3 gives the energy elements of the second-order pertubation for J=3 and 4 with I=1 of the symmetric and asymmetric rotors. The magnitudes for the symmetric tops have been calculated by the numerator in Eq. (10), and those for the asymmetric rotors have been calculated by the numerator in Eq. (14). The first two columns indicate the allowed values of F, the third one indicates the sub-quantum numbers of the lower value of F. The forth one indicates the allowed values of K, the fifth and sixth indicate the energy elements for the symmetric and asymmetric rotors. The expression for the line strengths of the asymmetric rotors is the same as the numerator in Eq. (14), so that the magnitude in the last column may be used for the line strengths of the asymmetric rotors.

4. Comparsions of Line Strengths and Energy Elements of the Ammonia Inversion Spectrum

The calculations of the Stark effect with hyperfine structure for the ammonia inversion spectrum have been shown in Ref. 1. The magnitudes of the energy matrix elements and relative intensities were computed only by considering

the diagonal part. But as a matter of fact, the off-diagonal elements are effective. The exact energy levels should be obtained by diagonalizing the matrix established by Eq. (5) and line strengths should be computed by Eq. (9). The calculated exact energy elements and line strengths are shown in Tables 4 and 5. We found that the number of lines allowed in Table 5 is less than that in Table III in Ref. 1. When the energy matrix is diagonalized, any new state will be mixed by the original ones. The line strength between any two new states will be interferred by the original ones, some are interferred constructively and some destructively, consequently several transition lines will be forbidden. This will not be found by only considering the diagonal part. For comparsions, the line strengths computed by Eq. (8) and the relative intensities used in Ref. 1 are shown in Table 6. The ratio of relative intensity to the line strength for each component is 5.25, which is the pure rotational relative intensity

$$(2J+1)(2J'+1) \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix}^2 = (2\times3+1)(2\times3+1) \begin{pmatrix} 3 & 1 & 3 \\ 3 & 0 & -3 \end{pmatrix}^2 .$$

IV. Conclusions

According to comparsions shown in III-4, we realized it is a real fact that we can not only use the formulas presented in text to express and calculate the energy matrix elements easily, but also obtain the line strengths correctly. The procedures for the treatment of the Stark effect with hyperfine structure may be further extended to the multiple quadrupole nuclei cases. The treatment of the relative intensities in terms of 3j symbols for the symmetric tops might be extended to that of the asymmetric rotors, then the calculation of the relative intensities in terms of 3j symbols will be much more convenient than the conventional method.

Table 1. The exact energy elements and eigenvectors of Stark effect with hyperfine structure of symmetric rotor for J=4, K=3, and I=1.0 .

J= 4	K= 3	I= 1.0	
EIGENVALUE		EIGENVECTORS	
F=	5.0	4.0	3.0
MF= 5.0			
-0.600000	1.000000		
MF= 4.0			
-0.450000	0.894427	-0.447214	
-0.600000	0.447214	0.894427	
MF= 3.0			
-0.300000	0.788811	-0.591608	0.166667
-0.450000	0.596285	0.670820	-0.440959
-0.600000	0.149071	0.447214	0.881917
MF= 2.0			
-0.150000	0.683130	-0.670820	0.288675
-0.300000	0.683130	0.447214	-0.577350
-0.450000	0.258199	0.591608	0.763763
MF= 1.0			
0.000000	0.577350	-0.707107	0.408248
-0.150000	-0.730297	-0.223607	0.645497
-0.300000	0.365148	0.670820	0.645497

	MF= 0.0		
	0.150000	0.471405	-0.707107	0.527046
	0.000000	-0.745356	0.000000	0.666667
	-0.150000	0.471405	0.707107	0.527046

	MF= -1.0		
	0.300000	-0.365148	0.670820	-0.645497
	0.150000	-0.730297	0.223607	0.645497
	0.000000	0.577350	0.707107	0.408248

	MF= -2.0		
	0.450000	0.258199	-0.591608	0.763763
	0.300000	-0.683130	0.447214	0.577350
	0.150000	0.683130	0.670820	0.288675

	MF= -3.0		
	0.600000	0.149071	-0.447214	0.881917
	0.450000	-0.596285	0.670820	0.440959
	0.300000	0.788811	0.591608	0.166667

	MF= -4.0		
	0.600000	-0.447214	0.894427
	0.450000	0.894427	0.447214

	MF= -5.0	
	0.600000	1.000000

Table 2. The line strengths of Stark effect with hyperfine structure for J=3 and I=1.

I= 1.0

JL	MFL		JU	MFU	INTENS.	EIGENVALUES		ΔJ
3	4.0	-	3	4.0	0.10714	-0.750000	-0.750000	0
3	4.0	-	4	4.0	0.02778	-0.750000	-0.450000	1
3	3.0	-	3	3.0	0.04762	-0.500000	-0.500000	0
3	3.0	-	4	3.0	0.04762	-0.500000	-0.300000	1
3	3.0	-	3	3.0	0.10714	-0.750000	-0.750000	0
3	3.0	-	4	3.0	0.02778	-0.750000	-0.450000	1
3	2.0	-	3	2.0	0.01190	-0.250000	-0.250000	0
3	2.0	-	4	2.0	0.05952	-0.250000	-0.150000	1
3	2.0	-	3	2.0	0.04762	-0.500000	-0.500000	0
3	2.0	-	4	2.0	0.04762	-0.500000	-0.300000	1
3	2.0	-	3	2.0	0.10714	-0.750000	-0.750000	0
3	2.0	-	4	2.0	0.02778	-0.750000	-0.450000	1
3	1.0	-	4	1.0	0.06349	-0.000000	0.000000	1
3	1.0	-	3	1.0	0.01190	-0.250000	-0.250000	0
3	1.0	-	4	1.0	0.05952	-0.250000	-0.150000	1
3	1.0	-	3	1.0	0.04762	-0.500000	-0.500000	0
3	1.0	-	4	1.0	0.04762	-0.500000	-0.300000	1
3	0.0	-	3	0.0	0.01190	0.250000	0.250000	0
3	0.0	-	4	0.0	0.05952	0.250000	0.150000	1
3	0.0	--	4	0.0	0.06349	0.000000	0.000000	1
3	0.0	-	3	0.0	0.01190	-0.250000	-0.250000	0
3	0.0	-	4	0.0	0.05952	-0.250000	-0.150000	1
3	-1.0	-	3	-1.0	0.04762	0.500000	0.500000	0
3	-1.0	-	4	-1.0	0.04762	0.500000	0.300000	1
3	-1.0	-	3	-1.0	0.01190	0.250000	0.250000	0
3	-1.0	-	4	-1.0	0.05952	0.250000	0.150000	1
3	-1.0	-	4	-1.0	0.06349	0.000000	-0.000000	1
3	-2.0	-	3	-2.0	0.10714	0.750000	0.750000	0

3	-2.0	-	4	-2.0	0.02778	0.750000	0.450000	1
3	-2.0	-	3	-2.0	0.04762	0.500000	0.500000	0
3	-2.0	-	4	-2.0	0.04762	0.500000	0.300000	1
3	-2.0	-	3	-2.0	0.01190	0.250000	0.250000	0
3	-2.0	-	4	-2.0	0.05952	0.250000	0.150000	1
3	-3.0	-	3	-3.0	0.10714	0.750000	0.750000	0
3	-3.0	-	4	-3.0	0.02778	0.750000	0.450000	1
3	-3.0	-	3	-3.0	0.04762	0.500000	0.500000	0
3	-3.0	-	4	-3.0	0.04762	0.500000	0.300000	1
3	-4.0	-	3	-4.0	0.10714	0.750000	0.750000	0
3	-4.0	-	4	-4.0	0.02778	0.750000	0.450000	1

Table 3. The energy elements of the second-order perturbation of symmetric and asymmetric
rotors for J=3 and 4 with I=1.

JL=3   JU=4   I= 1.0

FL	FU	MF	K	SYM	ASYM
4.0	5.0	4.0			0.022222
			0	0.088889	
			1	0.083333	
			2	0.066667	
			3	0.038889	
4.0	5.0	3.0			0.039506
			0	0.158025	
			1	0.148148	
			2	0.118519	
			3	0.069136	
4.0	5.0	2.0			0.051852
			0	0.207407	
			1	0.194444	
			2	0.155556	
			3	0.090741	
4.0	5.0	1.0			0.059259
			0	0.237037	
			1	0.222222	
			2	0.177778	
			3	0.103704	
4.0	5.0	0.0			0.061728
			0	0.246914	
			1	0.231481	
			2	0.185185	
			3	0.108025	
4.0	4.0	4.0			0.005556
			0	0.022222	
			1	0.020833	
			2	0.016667	
			3	0.009722	
4.0	4.0	3.0			0.003125
			0	0.012500	
			1	0.011719	
			2	0.009375	
			3	0.005469	
4.0	4.0	2.0			0.001389
			0	0.005556	
			1	0.005208	
			2	0.004167	
			3	0.002431	

4.0	4.0	1.0			0.000347
			0	0.001389	
			1	0.001302	
			2	0.001042	
			3	0.000608	
4.0	3.0	3.0			0.000028
			0	0.000110	
			1	0.000103	
			2	0.000083	
			3	0.000048	
4.0	3.0	2.0			0.000047
			0	0.000189	
			1	0.000177	
			2	0.000142	
			3	0.000083	
4.0	3.0	1.0			0.000059
			0	0.000236	
			1	0.000221	
			2	0.000177	
			3	0.000103	
4.0	3.0	0.0			0.000063
			0	0.000252	
			1	0.000236	
			2	0.000189	
			3	0.000110	
3.0	4.0	3.0			0.026042
			0	0.104167	
			1	0.097656	
			2	0.078125	
			3	0.045573	
3.0	4.0	2.0			0.044643
			0	0.178571	
			1	0.167411	
			2	0.133929	
			3	0.078125	
3.0	4.0	1.0			0.055804
			0	0.223214	
			1	0.209263	
			2	0.167411	
			3	0.097656	
3.0	4.0	0.0			0.059524
			0	0.238095	
			1	0.223214	
			2	0.178571	
			3	0.104167	
3.0	3.0	3.0			0.006696
			0	0.026786	
			1	0.025112	
			2	0.020089	
			3	0.011719	
3.0	3.0	2.0			0.002976
			0	0.011905	
			1	0.011161	
			2	0.008929	
			3	0.005208	

2.0	3.0	1.0				0.000744
				0	0.002976	
				1	0.002790	
				2	0.002232	
				3	0.001302	
2.0	3.0	2.0				0.034014
				0	0.136054	
				1	0.127551	
				2	0.102041	
				3	0.059524	
2.0	3.0	1.0				0.054422
				0	0.217687	
				1	0.204082	
				2	0.163265	
				3	0.095238	
2.0	3.0	0.0				0.061224
				0	0.244898	
				1	0.229592	
				2	0.183673	
				3	0.107143	

Table 4. The exact energy elements and eigenvectors of the Stark effect with hyperfine structure of ammonia inversion spectrum at J=3 and K=3.

EIGENVALUE	EIGENVECTORS		
F=	4.0	3.0	2.0
MF= 4.0			
-0.750000	1.000000		
MF= 3.0			
-0.500000	0.866025	-0.500000	
-0.750000	0.500000	0.866025	
MF= 2.0			
-0.250000	0.731925	-0.645497	0.218218
-0.500000	0.654654	0.577350	-0.487950
-0.750000	0.188982	0.500000	0.845154
MF= 1.0			
-0.000000	0.597614	-0.707107	0.377964
-0.250000	0.731925	0.288675	-0.617213
-0.500000	0.327327	0.645497	0.690066
MF= 0.0			
0.250000	0.462910	-0.707107	0.534523
0.000000	-0.755929	-0.000000	0.654654
-0.250000	0.462910	0.707107	0.534522
MF= -1.0			
0.500000	0.327327	-0.645497	0.690066
0.250000	-0.731925	0.288675	0.617213
0.000000	0.597614	0.707107	0.377964
MF= -2.0			
0.750000	0.188982	-0.500000	0.845154
0.500000	-0.654654	0.577350	0.487950
0.250000	0.731925	0.645497	0.218218

MF= -3.0
| 0.750000 | -0.500000 | 0.866025 |
| 0.500000 | 0.866025 | 0.500000 |

MF= -4.0
| 0.750000 | 1.000000 | |

Table 5. The line strengths of Stark effect with hyperfine structure of ammonia inversion spectrum at J=3 and K=3.

JL	MFL	JU	MFU	INTENS	EIGENVALUES	
3	4	3	4	0.10714	-0.750000	-0.750000
3	3	3	3	0.04762	-0.500000	-0.500000
3	3	3	3	0.10714	-0.750000	-0.750000
3	2	3	2	0.01190	-0.250000	-0.250000
3	2	3	2	0.04762	-0.500000	-0.500000
3	2	3	2	0.10714	-0.750000	-0.750000
3	1	3	1	0.01190	-0.250000	-0.250000
3	1	3	1	0.04762	-0.500000	-0.500000
3	0	3	0	0.01190	-0.250000	-0.250000
3	0	3	0	0.01190	-0.250000	-0.250000

Table 6. The relative intensities of Stark effect with hyperfine structure of ammonia inversion spectrum calculated in Ref. 1 and line strengths computed by Eq. (8) shown in this work.

Initial		Final		Relative	Line
F	M	F	M	Intensity	Strength
4	4	4	4	0.563	0.10714
4	3	4	3	0.316	0.06027
4	2	4	2	0.141	0.02679
4	1	4	1	0.035	0.00670
3	3	3	3	0.473	0.09003
3	2	3	2	0.210	0.04001
3	1	3	1	0.053	0.01000
2	2	2	2	0.444	0.08466
2	1	2	1	0.111	0.02116
4	3	3	3	0.0117	0.00223
4	2	3	2	0.0201	0.00383
4	1	3	1	0.0251	0.00478
4	0	-3	0	0.0268	0.00510
3	2	2	2	0.0198	0.00378
3	1	2	1	0.0317	0.00605
3	0	2	0	0.0357	0.00680
2	2	3	2	0.0198	0.00378
2	1	3	1	0.0317	0.00605
2	0	3	0	0.0357	0.00680
3	3	4	3	0.0117	0.00223
3	2	4	2	0.0201	0.00383
3	1	4	1	0.0251	0.00478
3	0	4	0	0.0268	0.00510

Appendix

The explicit form in terms of 3j symbols for the relative intensity of the symmetric tops.

For the symmetric rotor, the dipole moment directed along the space-fixed Z axis is given by

$$\mu_Z = \mu_z \; \phi_{Zz} \; , \tag{A1}$$

where μ_z is the dipole moment directed along the body-fixed symmetry z axis, and ϕ_{Zz} the direction cosine between Z and z-axes. If we use the spherical form, we can rewrite Eq. (A1) as

$$\mu_0^{(1)} = \mu_0 \, D_{00}^{(1)} \; , \tag{A2}$$

where the expression $D_{00}^{(1)}$, the first-order rotational representation, is equivalent to ϕ_{Zz}[19]. The subscript of μ may be dropped to give

$$\mu_0^{(1)} = \mu \, D_{00}^{(1)} \; . \tag{A3}$$

The matrix elements between two symmetric top wave functions will be

$$< J'K'M_J' \mid \mu_0^{(1)} \mid JKM_J > \; = \; \mu < J'K'M_J' \mid D_{00}^{(1)} \mid JKM_J > \; .$$

Using Eq. (1) and the integration of 3 D's [20], we obtain the matrix elements for both sides of the equation above as

$$< J'K'M_J' \mid \mu_0 \mid JKM_J > \; = (-1)^{J'-M_J'} < J'K' \| \mu^{(1)} \| JK >$$

$$\times \begin{pmatrix} J' & 1 & J \\ -M_J' & 0 & M_J \end{pmatrix} \; , \tag{A4}$$

and

$$< J'K'M_J' \mid \mu \, D_{00}^{(1)} \mid JKM > \; = \mu \, (-1)^{M_J-K} \, [(2J'+1)(2J+1)]^{1/2}$$

$$\times \begin{pmatrix} J & 1 & J' \\ M_J & 0 & -M_J' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix} \tag{A5}$$

Using the symmetry property of 3j symbols and equating Eqs. (A4) and (A5), we get the reduced matrix element as

$$< J'K' \| \mu^{(1)} \| JK > \; = \mu \, (-1)^{J+1-K-M_J'+M_J} \, [(2J+1)(2J'+1)]$$

$$\times \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix}$$

For non-vanishing matrix elements, it is required that M_J be equal to M_J', then the equation above may be reduced to

$$< J'K' \| \mu^{(1)} \| JK > = \mu (-1)^{J+1-K} [(2J'+1)(2J+1)]^{1/2} \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix}, \qquad (A6)$$

the same expression has be used in Ref. 10. The square of the matrix elements of Eq. (A6) is the relative intensity of rotational transition, it is

$$< J'K' \| \mu^{(1)} \| JK > |^2 = \mu^2 (2J'+1)(2J+1) \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix}^2. \qquad (A7)$$

The selection rules are $\Delta J = 0, \pm 1$ and $\Delta K = 0$.

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