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張量演算子對史托克效應的應用
Application of Spherical Tensor Operator to Stark Effect

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Abstract — The expressions of the energy levels and line strengths of the Stark effect for both symmetric and asymmetric rotors have been derived by employing the spherical tensor operator and first-order rotational representations. The application of the Wigner-Eckart theorem have been briefly discussed. The magnitudes of the energy matrix elements for first and second-orders and line strengths of J up to 4 of the symmetric tops have been tabulated. Some experimental measurements have been discussed.

I. Introduction

In the previous works [1, 2], the expressions in terms of 3j symbols for the pure rotational transition line strengths have been derived for both symmetric and asymmetric rotors. The concept set forth there is to use the relations of the linear combinations between the direction cosines and the first-order rotational representations. Both, functions of the Euler's angles, are generally used to express the geometric relations between the space-fixed frame and body-fixed frame respectively in the cartesian coordinates and the spherical coordinates. It is found that the calculations and derivations in terms of the tensor operator algebra are much easier and more convenient than the traditional methods in cartesian forms [3-5]. It is feasible and worthwhile to further extend this kind of special and useful algebra to the case of Stark effect. Stark effect is due to the interaction between the permanent dipole moment in the body-fixed frame and the external electric field in the space-fixed frame. So that the dipole moment, electric field, wave functions of the rotational energy levels, and direction cosines are the most essential elements. Recently the spherical tensor operator has been used for the Stark effect of the symmetric tops [6, 7]. The explicit forms are in terms of 3j symbols. In order to reduce the laborious calculations of the Stark effect for asymmetric rotors, a several processes have been established [8-11]. They do not, in fact, help too much. The reason is that they don't reduce the formulas any more. The purpose of this paper is to used the first-order rotational representations and the wave functions in rotational representations to establish the expressions of the energy levels and line strengths of the Stark effect for the asymmetric rotors. The explicit forms are in 3j symbols. The same procedure used for that of the symmetric tops and the application of the Wigner-Eckart theorem for both cases will be briefly discussed. The comparsions between the experimental data and our calculated results are also presented.

II. Derivation

The Hamiltoman of Stark effect is given as

$$H = -\bar{\mu} \cdot \bar{E},$$

where $\bar{\mu}$ is the permanent dipole moment in the body-fixed frame and E is the external electric field in the space-fixed frame.

1. Symmetric tops

The dipole moment of a symmetric top is directed along the symmetry z axis, the interaction energy of $\bar{\mu}$ at an angle θ in an external electric field $\bar{E}$ is $-\mu E \cos\theta$. If we consider the direction cosine, the interaction energy may then the written as $-\mu E \Phi_{Zz}$ or $-\mu_Z E$, where Φ_{Zz} is the direction cosine between Z and z-axes and μ_Z the dipole moment component along Z-axis. Replacing the direction cosine Φ_{Zz} by its equivalent rotational representation $D^{(1)}_{oo}$ shown in Ref. 2, we may write the energy as $-\mu E D^{(1)}_{oo}$. The expression $-\mu D^{(1)}_{oo}$ is equivalent to $\mu^{(1)}_o$, which is the spherical form of the dipole moment component along the space-fixed Z-axis. The wave functions of symmetric tops used for the Stark effect are $|JKM>$, where J stands for rotational quantum number, K and M the projection quantum numbers respectively along z and Z-axes. The first-order perturbation energy matrix elements are

$$<J'K'M'|-\mu E D^{(1)}_{oo}|JKM> \text{ or } <J'K'M'|-\mu^{(1)}_o E|JKM>$$

Following the integration of three D's [12, 13]

$$<J'K'M'|D^{(k)}_{qq'}|JKM> = (-1)^{M-K}[(2J'+1)(2J+1)]^{1/2}\begin{pmatrix} J & K & J' \\ M & -q & -M' \end{pmatrix}\begin{pmatrix} J & K & J' \\ K & -q & -K' \end{pmatrix}, \quad (1)$$

we have the matrix elements as

$$<J'K'M'|-\mu E D^{(1)}_{oo}|JKM> = -\mu E(-1)^{M-K}[(2J'+1)(2J+1)]^{1/2}$$

$$\times \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix}\begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix} \quad (2)$$

If we consider the Wigner-Eckart theorem [14]

$$<\alpha'J'K'M'|T^{(k)}|\alpha JKM> = (-1)^{J'-K'}\begin{pmatrix} J' & k & J \\ -M' & q & M \end{pmatrix}$$

$$\times <\alpha'J'K'||T^{(k)}||\alpha JK>, \quad (3)$$

then we obtain the matrix elements of $-\mu^{(1)}_o E$ as

$$<J'K'M'|-\mu^{(1)}_o E|JKM> = (-1)^{J'-M'}(-E)\begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix} <J'K'||\mu^{(1)}||JK>. \quad (4)$$

The reduced matrix element in Eq. (4) represents the dipole moment matrix element in symmetric top [1, 6], and its square represents the line strength of pure rotational transition. Combining the explicit form of the reduced matrix element

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

interchanging the proper columns, we may write Eq. (4) as

$$< J'K'M' |-\mu_o^{(1)} E|JKM> = -\mu E(-1)^{-K-M}[(2J'+1)(2J+1)]^{1/2} \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix} \times \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix} \quad (5)$$

Since K and M are integers, the phase in Eq. (2) will be equal to that in Eq. (5). Consequently both equations are equivalent. Considering theenergy levels of the Stark effect for a given rotational state $|JK>$ and using $\begin{pmatrix} J & J & 1 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M} \frac{M}{[(2J+1)(J+1)]^{1/2}}$, then we have the frist-order splitting energies

$$E_{JKM}^{(1)} = -\mu E \frac{KM}{J(J+1)} \quad (6)$$

The relative intensity of the Stark effect for a symmetric top is defined as the square of the dipole moment matrix elements between two states $|J'K'M'>$ and $|JKM>$, it is

$$S(J'K'M' \to JKM) = | < J'K'M' | \mu_Z | JKM> |^2 .$$

By use of the equivalent $\mu D_{oo}^{(1)}$ of μ_Z, the intensity may be written as

$$S(J'K'M' \to JKM) = |\mu < J'K'M' | D_{oo}^{(1)} | JKM> |^2 , \quad (7)$$

and by use of Eq.(1), the expression shown above may then be written as

$$S(J'K'M' \to JKM) = [\mu^2(2J'+1)(2J+1) \begin{pmatrix} J & 1 & J' \\ K & 0 & -K' \end{pmatrix}^2] \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix}^2 \quad (8)$$

The expression in the bracket [ ] apparently stands for the line strength of the pure rotational transition for a symmetric top, and it can be omitted for a certain rotational transition line. For simplicity, the line strength of Stark effect may be written as

$$S(J'K'M' \to JKM) = \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix}^2 \quad (9)$$

From Eq. (9) we find the selection rules are $\Delta M=0$. When M=0, only the cases of $J' - J = \pm 1$ are allowable.

Once the first-order correction is not adequately accurate, the second-order correction is needed. The general form for the second-order perturbation is

$$E_{JKM}^{(2)} = \sum_{J'K'} \frac{\mu^2 E^2 \, | < JKM | D_{oo}^{(1)} | J'K'M' > |^2}{E_{JK}^{(0)} - E_{J'K'}^{(0)}}$$

From the definition of the relative intensity of the Stark effect and Eq. (7), we realize that the absolute value in the numerator of the equation shown above stands for nothing but the relative intensity of Stark effect line between the states $|J'K'M'>$ and $|JKM>$. In order to obtain the non-zero terms in the numerator and to avoid the zero

term in the denominator, we find that only those terms, containing $\Delta K=0$, $\Delta M=0$, and $\Delta J=\pm 1$, contribute to $E^{(2)}_{JKM}$. Using the rotational energy $E_{JK}=[BJ(J+1)+(A-B)K^2]$ for each specified state, we get the second-order energy conection

$$E^{(2)}_{JKM}=\left[\frac{(2J+1)(2J+3)\begin{pmatrix} J+1 & 1 & J \\ M & 0 & M \end{pmatrix}^2 \begin{pmatrix} J+1 & 1 & J \\ K & 0 & -K \end{pmatrix}^2}{J(J+1)-(J+1)(J+2)}\right.$$

$$\left.+\frac{(2J+1)(2J-1)\begin{pmatrix} J-1 & 1 & J \\ M & 0 & -M \end{pmatrix}^2 \begin{pmatrix} J-1 & 1 & J \\ K & 0 & -K \end{pmatrix}^2}{J(J+1)-(J-1)(J)}\right]\frac{\mu^2E^2}{B} \quad . \tag{10}$$

By use of the equivalent of 3j symbols, the equation shown above may be rewritten as

$$E^{(2)}_{JKM}=\frac{\mu^2E^2}{2B}\left\{-\frac{[(J+1)^2-K^2]\,[(J+1)^2-M^2]}{(J+1)^3(2J+3)(2J+1)}+\frac{(J^2-K^2)(J^2-M^2)}{J^3(2J+1)(2J-1)}\right\} \quad . \tag{11}$$

Where B is the rotational constant of a symmetric top. Equation (11) has been used widely and recently derived by means of the spherical tensor operator algebra in Ref. 7.

2. Asymmetric rotors

The first-order Hamiltonian operator of a asymmetric rotor is given by

$$H^{(1)}=-\ \mu\cdot E=-E\sum_g \mu_g\ \Phi_{Zg}\ , \tag{12}$$

where E is the external electric field directed along the space-fixed Z axis, and μ_g is the permanent dipole moment component directed along the body-fixed g axis. Applying the perturbation theory in evaluating the matrix element of Eq. (12), we have to use the asymmetric rotor wave functions, which are expressed as the linear combination of the symmetric top basis. These two kinds of wave functions have the same J and M. The main process for the Stark effect energy levels is to obtain the direction cosine matrix elements between two energy levels $|J'\tau'M'>$ and $|J\tau M>$. It was found that there were no-diagonal matrix elements for $H^{(1)}$ by considering the symmetry properties of the Four group in Ref. 8. This means there is no first-order conection energy of the Stark effect for an asymmetric rotor.

For the second-order pertubation, the general form of the energy correction is given as

$$E^{(2)}_{J\tau M}=\sum_g \mu_g^2E^2\sum_{J'\tau'}\frac{|<J\tau M|\ \Phi_{Zg}|J'\tau'M'>|^2}{E^{(0)}_{J\tau}-E^{(0)}_{J'\tau'}}\ , \tag{13}$$

where the summation is to extend only over those values of $E^{(0)}_{J\tau}$ for which $E^{(0)}_{J'\tau'}$ is not near $E^{(0)}_{J\tau}$. Replacing Φ_{Zg}, say g=z, by its rotational representation $D^{(1)}_{oo}$, and taking the linear combination forms of $|J\tau M>$ and $|J'\tau'M'>$, we obtain the expression for the numerator in Eq. (13) as

$$|<J'\tau'M'|\ \Phi_{Zz}|J\tau M>|^2=|\sum_{ij}C_iC_j<JK_jM|D^{(1)}_{oo}|J'K_iM'>|^2 \ . \tag{14}$$

Where C_i and C_j are the linear combination coefficients of the Wang wave functions. The method of obtaining C_i and C_j has been discussed by King et al [15]. Using Eq. (1), we obtain the explicit form in terms of 3j symbols for

Eq. (14) as

$$|\langle J'\tau'M'|\Phi_{Zz}|J\tau M\rangle|^2 = \left[(2J'+1)(2J+1)\left|\sum_{ij} C_i C_j \begin{pmatrix} J & 1 & J' \\ K_j & 0 & -K_i \end{pmatrix}\right|^2\right]$$

$$\times \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix} , \qquad (15)$$

where the expression in the bracket [ ] stands for the line strength along z-axis as shown in Ref. 2, which is regularly expressed by λ_z. For non-vanishing matrix elements, the value of M shall be equal to that of M'. Combining Eqs. (13) and (15) and using λ_z for the line strength, we obtain the expression along z-axis as

$$(E^{(2)}_{J\tau M})_z = \sum_{J'\tau'} \frac{\mu_z^2 \lambda_z \begin{pmatrix} J & 1 & J' \\ M & 0 & -M \end{pmatrix}^2}{E^{(0)}_{J\tau} - E^{(0)}_{J'\tau'}} \qquad (16)$$

By use of the same procedure, the expressions of the contributions due to the other two axes will be

$$(E^{(2)}_{J\tau M})_x = \sum_{J'\tau'} \frac{\mu_x^2 \lambda_x \begin{pmatrix} J & 1 & J' \\ M & 0 & -M \end{pmatrix}^2}{E^{(0)}_{J\tau} - E^{(0)}_{J'\tau'}} \quad . \qquad (17)$$

and

$$(E^{(2)}_{J\tau M})_y = \sum_{J'\tau'} \frac{\mu_y^2 \lambda_y \begin{pmatrix} J & 1 & J' \\ M & 0 & -M \end{pmatrix}^2}{E^{(0)}_{J\tau} - E^{(0)}_{J'\tau'}} \quad . \qquad (18)$$

The total contribution will be the summation of Eqs. (16), (17), and (18), it is

$$E^{(2)}_{J\tau M} = E^2 \sum_{gJ'\tau'} \frac{\mu_g^2 \lambda_g \begin{pmatrix} J & 1 & J' \\ M & 0 & -M \end{pmatrix}^2}{E^{(0)}_{J\tau} - E^{(0)}_{J'\tau'}} \quad . \qquad (19)$$

The relative intensity of the Stark effect for the asymmetric rotors is defined as the square of the dipole moment matrix elements between two states $|J\tau M\rangle$ and $|J'\tau'M'\rangle$, it is

$$S(J'\tau'M' \to J\tau M) = |\langle J'\tau'M'|\mu_Z(\mu_O^{(1)})|J\tau M\rangle|^2 .$$

For specifying the axis to which μ_z is due, it is more suitable to rewrite the above equation as

$$S_Z(J'\tau'M' \to J\tau M) = \mu_z^2 |\langle J'\tau'M'|\Phi_{Zz}|J\tau M\rangle|^2 .$$

where the square of the absolute value is equivalent to Eq. (15), which involves the line strength along z-axis and the projection part. The rotational line strength may be dropped for the Stark effect, so that the line strength for Stark effect is

$$S(J'\tau'M' \rightarrow J\tau M) = \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix}^2 \quad (20)$$

III. Results and Discussions

The energy elements of the frist-order perturbation for the symmetric tops have been calculated for J up to 4 by Eq. (2). The magnitudes with the proper quantum numbers are given in Table 1.

Table 1. Energy elements of frist-order perturbation for J up 4.

J	K	JK (3j)	M	JM (3J)	ELEMENT
1					
	1	-0.4082483			
			-1	0.4082483	0.5000000
			0	0.0000000	0.0000000
			1	-0.4082483	-0.5000000
2					
	1	0.1825742			
			-2	0.3651484	0.3333333
			-1	-0.1825742	0.1666667
			0	0.0000000	0.0000000
			1	0.1825742	-0.1666667
			2	-0.3651484	-0.3333333
	2	-0.3651484			
			-2	0.3651484	0.6666667
			-1	-0.1825742	0.3333333
			0	0.0000000	0.0000000
			1	0.1825742	-0.3333333
			2	-0.3651484	-0.6666667
3					
	1	-0.1091089			
			-3	0.3273268	0.2500000
			-2	-0.2182179	0.1666667
			-1	0.1091089	0.0833333
			0	0.0000000	0.0000000
			1	-0.1091089	-0.0833333
			2	0.2182179	-0.1666667
			3	-0.3273268	-0.2500000
	2	0.2182179			
			-3	0.3273268	0.5000000
			-2	-0.2182179	0.3333333
			-1	0.1091089	0.1666667
			0	0.0000000	0.0000000
			1	-0.1091089	-0.1666667
			2	0.2182179	-0.3333333
			3	-0.3273268	-0.5000000
	3	-0.3273268			
			-3	0.3273268	0.7500000
			-2	-0.2182179	0.5000000
			-1	0.1091089	0.2500000
			0	0.0000000	0.0000000
			1	-0.1091089	-0.2500000
			2	0.2182179	-0.5000000
			3	-0.3273268	-0.7500000

4					
	1	0.0745356			
			-4	0.2981424	0.2000000
			-3	-0.2236068	0.1500000
			-2	0.1490712	0.1000000
			-1	-0.0745356	0.0500000
			0	0.0000000	0.0000000
			1	0.0745356	-0.0500000
			2	-0.1490712	-0.1000000
			3	0.2236068	-0.1500000
			4	-0.2981424	-0.2000000
	2	-0.1490712			
			-4	0.2981424	0.4000000
			-3	-0.2236068	0.3000000
			-2	0.1490712	0.2000000
			-1	-0.0745356	0.1000000
			0	0.0000000	0.0000000
			1	0.0745356	-0.1000000
			2	-0.1490712	-0.2000000
			3	0.2236068	-0.3000000
			4	-0.2981424	-0.4000000
	3	0.2236068			
			-4	0.2981424	0.6000000
			-3	-0.2236068	0.4500000
			-2	0.1490712	0.3000000
			-1	-0.0745356	0.1500000
			0	0.0000000	0.0000000
			1	0.0745356	-0.1500000
			2	-0.1490712	-0.3000000
			3	0.2236068	-0.4500000
			4	-0.2981424	-0.6000000
	4	-0.2981424			
			-4	0.2981424	0.8000000
			-3	-0.2236068	0.6000000
			-2	0.1490712	0.4000000
			-1	-0.0745356	0.2000000
			0	0.0000000	0.0000000
			1	0.0745356	-0.2000000
			2	-0.1490712	-0.4000000
			3	0.2236068	-0.6000000
			4	-0.2981424	-0.8000000

The first column represents the rotational quantum number J, the second one the sub-quantum number K in body-fixed frame, the third one the value of 3j symbols involving J's and K's, the forth one the sub-quantum number M in space-fixed frame, the fifth one the value of 3j symbols involving J's and M's, and the last one the energy matrix element. The real energy shift in MHz shall be the multiplication of these elements E (V/cm), μ (Debye), and conversion factor 0.50348. The spacings between any two energy levels of Stark effect are equal.

Table 2. Line strengths for Stark effect.

1	1					
	0	0.00000				
			-1	0.0000000	0.0000000	0.0000000	0.16667
			0	0.0000000	0.0000000	0.0000000	0.00000
			1	0.0000000	0.0000000	0.0000000	0.16667

		1	1.50000					
				-1	0.5000000	0.5000000	0.0000000	0.16667
				0	0.0000000	0.0000000	0.0000000	0.00000
				1	-0.5000000	-0.5000000	0.0000000	0.16667
1	2							
		0	2.00000					
				-1	0.0000000	0.0000000	0.0000000	0.10000
				0	0.0000000	0.0000000	0.0000000	0.13333
				1	0.0000000	0.0000000	0.0000000	0.10000
		1	1.50000					
				-1	0.5000000	0.1666667	-0.3333333	0.10000
				0	0.0000000	0.0000000	0.0000000	0.13333
				1	-0.5000000	-0.1666667	0.3333333	0.10000
2	2							
		0	0.00000					
				-2	0.0000000	0.0000000	0.0000000	0.13333
				-1	0.0000000	0.0000000	0.0000000	0.03333
				0	0.0000000	0.0000000	0.0000000	0.00000
				1	0.0000000	0.0000000	0.0000000	0.03333
				2	0.0000000	0.0000000	0.0000000	0.13333
		1	0.83333					
				-2	0.3333333	0.3333333	0.0000000	0.13333
				-1	0.1666667	0.1666667	0.0000000	0.03333
				0	0.0000000	0.0000000	0.0000000	0.00000
				1	-0.1666667	-0.1666667	0.0000000	0.03333
				2	-0.3333333	-0.3333333	0.0000000	0.13333
		2	3.33333					
				-2	0.6666667	0.6666667	0.0000000	0.13333
				-1	0.3333333	0.3333333	0.0000000	0.03333
				0	0.0000000	0.0000000	0.0000000	0.00000
				1	-0.3333333	-0.3333333	0.0000000	0.03333
				2	-0.6666667	-0.6666667	0.0000000	0.13333
2	3							
		0	3.00000					
				-2	0.0000000	0.0000000	0.0000000	0.04762
				-1	0.0000000	0.0000000	0.0000000	0.07619
				0	0.0000000	0.0000000	0.0000000	0.08571
				1	0.0000000	0.0000000	0.0000000	0.07619
				2	0.0000000	0.0000000	0.0000000	0.04762
		1	2.66667					
				-2	0.3333333	0.1666667	-0.1666667	0.04762
				-1	0.1666667	0.0833333	-0.8333333	0.07619
				0	0.0000000	0.0000000	0.0000000	0.08571
				1	-0.1666667	-0.0833333	0.0833333	0.07619
				2	-0.3333333	-0.1666667	0.1666667	0.04762
		2	1.66667					
				-2	0.6666667	0.3333333	-0.3333333	0.04762
				-1	0.3333333	0.1666667	-0.1666667	0.07619
				0	0.0000000	0.0000000	0.0000000	0.08571
				1	-0.3333333	-0.1666667	0.1666667	0.07619
				2	-0.6666667	-0.3333333	0.3333333	0.04762
3	3							
		0	0.00000					
				-3	0.0000000	0.0000000	0.0000000	0.10714
				-2	0.0000000	0.0000000	0.0000000	0.04762
				-1	0.0000000	0.0000000	0.0000000	0.01190
				0	0.0000000	0.0000000	0.0000000	0.00000

				1	0.0000000	0.0000000	0.0000000	0.01190
				2	0.0000000	0.0000000	0.0000000	0.04762
				3	0.0000000	0.0000000	0.0000000	0.10714
		1	0.58333					
				-3	0.2500000	0.2500000	0.0000000	0.10714
				-2	0.1666667	0.1666667	0.0000000	0.04762
				-1	0.0833333	0.0833333	0.0000000	0.01190
				0	0.0000000	0.0000000	0.0000000	0.00000
				1	-0.0833333	-0.0833333	0.0000000	0.01190
				2	-0.1666667	-0.1666667	0.0000000	0.04762
				3	-0.2500000	-0.2500000	0.0000000	0.10714
		2	2.33333					
				-3	0.5000000	0.5000000	0.0000000	0.10714
				-2	0.3333333	0.3333333	0.0000000	0.04762
				-1	0.1666667	0.1666667	0.0000000	0.01190
				0	0.0000000	0.0000000	0.0000000	0.00000
				1	-0.1666667	-0.1666667	0.0000000	0.01190
				2	-0.3333333	-0.3333333	0.0000000	0.04762
				3	-0.5000000	-0.5000000	0.0000000	0.10714
		3	5.25000					
				-3	0.7500000	0.7500000	0.0000000	0.10714
				-2	0.5000000	0.5000000	0.0000000	0.04762
				-1	0.2500000	0.2500000	0.0000000	0.01190
				0	0.0000000	0.0000000	0.0000000	0.00000
				1	-0.2500000	-0.2500000	0.0000000	0.01190
				2	-0.5000000	-0.5000000	0.0000000	0.04762
				3	-0.7500000	-0.7500000	0.0000000	0.10714
3	4							
		0	4.00000					
				-3	0.0000000	0.0000000	0.0000000	0.02778
				-2	0.0000000	0.0000000	0.0000000	0.04762
				-1	0.0000000	0.0000000	0.0000000	0.05952
				0	0.0000000	0.0000000	0.0000000	0.06349
				1	0.0000000	0.0000000	0.0000000	0.05952
				2	0.0000000	0.0000000	0.0000000	0.04762
				3	0.0000000	0.0000000	0.0000000	0.02778
		1	3.75000					
				-3	0.2500000	0.1500000	-0.1000000	0.02778
				-2	0.1666667	0.1000000	-0.0666667	0.04762
				-1	0.0833333	0.0500000	-0.0333333	0.05952
				0	0.0000000	0.0000000	0.0000000	0.06349
				1	-0.0833333	-0.0500000	0.0333333	0.05952
				2	-0.1666667	-0.1000000	0.0666667	0.04762
				3	-0.2500000	-0.1500000	0.1000000	0.02778
		2	3.00000					
				-3	0.5000000	0.3000000	-0.2000000	0.02778
				-2	0.3333333	0.2000000	-0.1333333	0.04762
				-1	0.1666667	0.1000000	-0.0666667	0.05952
				0	0.0000000	0.0000000	0.0000000	0.06349
				1	-0.1666667	-0.1000000	0.0666667	0.05952
				2	-0.3333333	-0.2000000	0.1333333	0.04762
				3	-0.5000000	-0.3000000	0.2000000	0.02778
		3	1.75000					
				-3	0.7500000	0.4500000	-0.3000000	0.02778
				-2	0.5000000	0.3000000	-0.2000000	0.04762
				-1	0.2500000	0.1500000	-0.1000000	0.05952
				0	0.0000000	0.0000000	0.0000000	0.06349

			1	-0.2500000	-0.1500000	0.1000000	0.05952
			2	-0.5000000	-0.3000000	0.2000000	0.04762
			3	-0.7500000	-0.4500000	0.3000000	0.02778
4	4						
		0	0.00000				
			-4	0.0000000	0.0000000	0.0000000	0.08889
			-3	0.0000000	0.0000000	0.0000000	0.05000
			-2	0.0000000	0.0000000	0.0000000	0.02222
			-1	0.0000000	0.0000000	0.0000000	0.00556
			0	0.0000000	0.0000000	0.0000000	0.00000
			1	0.0000000	0.0000000	0.0000000	0.00556
			2	0.0000000	0.0000000	0.0000000	0.02222
			3	0.0000000	0.0000000	0.0000000	0.05000
			4	0.0000000	0.0000000	0.0000000	0.08889
		1	0.45000				
			-4	0.2000000	0.2000000	0.0000000	0.08889
			-3	0.1500000	0.1500000	0.0000000	0.05000
			-2	0.1000000	0.1000000	0.0000000	0.02222
			-1	0.0500000	0.0500000	0.0000000	0.00556
			0	0.0000000	0.0000000	0.0000000	0.00000
			1	-0.0500000	-0.0500000	0.0000000	0.00556
			2	-0.1000000	-0.1000000	0.0000000	0.02222
			3	-0.1500000	-0.1500000	0.0000000	0.05000
			4	-0.2000000	-0.2000000	0.0000000	0.08889
		2	1.80000				
			-4	0.4000000	0.4000000	0.0000000	0.08889
			-3	0.3000000	0.3000000	0.0000000	0.05000
			-2	0.2000000	0.2000000	0.0000000	0.02222
			-1	0.1000000	0.1000000	0.0000000	0.00556
			0	0.0000000	0.0000000	0.0000000	0.00000
			1	-0.1000000	-0.1000000	0.0000000	0.00556
			2	-0.2000000	-0.2000000	0.0000000	0.02222
			3	-0.3000000	-0.3000000	0.0000000	0.05000
			4	-0.4000000	-0.4000000	0.0000000	0.08889
		3	4.05000				
			-4	0.6000000	0.6000000	0.0000000	0.08889
			-3	0.4500000	0.4500000	0.0000000	0.05000
			-2	0.3000000	0.3000000	0.0000000	0.02222
			-1	0.1500000	0.1500000	0.0000000	0.00556
			0	0.0000000	0.0000000	0.0000000	0.00000
			1	-0.1500000	-0.1500000	0.0000000	0.00556
			2	-0.3000000	-0.3000000	0.0000000	0.02222
			3	-0.4500000	-0.4500000	0.0000000	0.05000
			4	-0.6000000	-0.6000000	0.0000000	0.08889
		4	7.20000				
			-4	0.8000000	0.8000000	0.0000000	0.08889
			-3	0.6000000	0.6000000	0.0000000	0.05000
			-2	0.4000000	0.4000000	0.0000000	0.02222
			-1	0.2000000	0.2000000	0.0000000	0.00556
			0	0.0000000	0.0000000	0.0000000	0.00000
			1	-0.2000000	-0.2000000	0.0000000	0.00556
			2	-0.4000000	-0.4000000	0.0000000	0.02222
			3	-0.6000000	-0.6000000	0.0000000	0.05000
			4	-0.8000000	-0.8000000	0.0000000	0.08889

Table 2 gives the line strengths of the Stark effect. The frist three columns stand for the allowed rotational transition

quantum numbers, lower J, upper J, and K, the forth one the rotational transition line strengths calculated by the part in bracket of Eq. (8),the fifth the allowed sub-quantum numbers M, the next two the energy shifts with respect to the lower and upper rotational states, the next one the shift element with respect to the rotational transition line, and the last one the line strength of the Stark effect calculated by Eq. (9). The real shift in MHz with respect to the rotational transition shall be the multiplication of shift element, E (V/cm), μ (Debye), and conversion factor. From Table 2 we realize that the spectral displacements due to Stark effect are symmetrically placed about the rotational transition line for both $\Delta J=1$ and 0. Starting from the rotational line, it is seen that the line strengths for the case $\Delta J=1$ are decreasing but those for the case $\Delta J=0$ are increasing. The pure rotation of the case $\Delta J=0$ does not exist. This is contrary to the case for the molecules having internal rotational [16] or inversion [17], it does. The frist-order Stark effect of CH_3OH due to internal rotation [17] have been observed. The magnitudes of line strengths calculated by Eq. (9) are tabulated in Table 3 and shown in Figure 1. The comparsion between the observed pattern and Figure 1 shows that the line strengths agree very well.

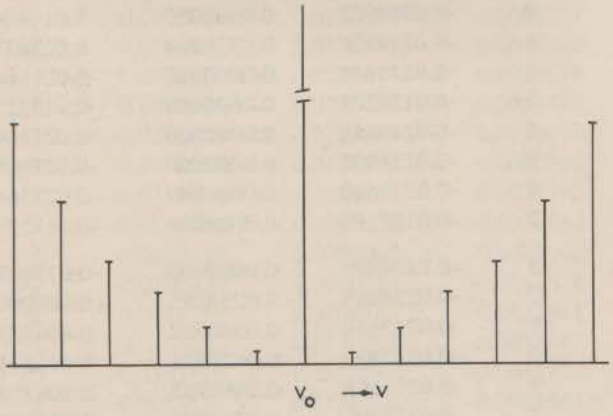

Figure 1. Pattern of line strengths and displacements of Stark effect of CH_3OH for J=6. The scale of frequency is arbitrary.

Table 3. Line strengths of Stark effect for CH_3OH.

M	Line Strength	Ratio
±1	0.00183	1.00
±2	0:00733	4.00
±3	0.01648	9.00
±4	0.02930	16.00
±5	0.04579	25.00
±6	0.06593	36.00

The second-order perturbation of symmetric tops have been computed by the expressions in bracket in Eq. (11) and given in Table 4. The first three columns represent rotational quantum number J, sub-quantum numbers K and M respectively, the forth one the contribution due to J+1 part, the fifth one the contribution due to J-1 part, and the last one the summation of those two. The real contribution in MH_z will be the multiplication of the last column, E^2, μ^2, reciprocial B (MH_z), and conversion factor $(0.50348)^2$.

Table 4. Energy elements of second-order perturbation for J up to 4 of symmetric tops.

J	K	M	J+1	J-1	SUM
0	0	0	-0.1666667	0.0000000	-0.1666667
1	0	-1	-0.0500000	0.0000000	-0.0500000
1	0	0	-0.0666667	0.1666667	0.1000000
1	0	1	-0.0500000	0.0000000	-0.0500000
1	1	-1	-0.0375000	0.0000000	-0.0375000
1	1	0	-0.0500000	0.0000000	-0.0500000
1	1	1	-0.0375000	0.0000000	-0.0375000
2	0	-2	-0.0238095	0.0000000	-0.0238095
2	0	-1	-0.0380952	0.0500000	0.0119048
2	0	0	-0.0428571	0.0666667	0.0238095
2	0	1	-0.0380952	0.0500000	0.0119048
2	0	2	-0.0238095	0.0000000	-0.0238095
2	1	-2	-0.0211640	0.0000000	-0.0211640
2	1	-1	-0.0338624	0.0375000	0.0036376
2	1	0	-0.0380952	0.0500000	0.0119048
2	1	1	-0.0338624	0.0375000	0.0036376
2	1	2	-0.0211640	0.0000000	-0.0211640
2	2	-2	-0.0132275	0.0000000	-0.0132275
2	2	-1	-0.0211640	0.0000000	-0.0211640
2	2	0	-0.0238095	0.0000000	-0.0238095
2	2	1	-0.0211640	0.0000000	-0.0211640
2	2	2	-0.0132275	0.0000000	-0.0132275
3	0	-3	-0.0138889	0.0000000	-0.0138889
3	0	-2	-0.0238095	0.0238095	0.0000000
3	0	-1	-0.0297619	0.0380952	0.0083333
3	0	0	-0.0317460	0.0428571	0.0111111
3	0	1	-0.0297619	0.0380952	0.0083333
3	0	2	-0.0238095	0.0238095	0.0000000
3	0	3	-0.0138889	0.0000000	-0.0138889
3	1	-3	-0.0130208	0.0000000	-0.0130208
3	1	-2	-0.0223214	0.0211640	-0.0011574
3	1	-1	-0.0279018	0.0338624	0.0059606
3	1	0	-0.0297619	0.0380952	0.0083333
3	1	1	-0.0279018	0.0338624	0.0059606
3	1	2	-0.0223214	0.0211640	-0.0011574
3	1	3	-0.0130208	0.0000000	-0.0130208
3	2	-3	-0.0104167	0.0000000	-0.0104167
3	2	-2	-0.0178571	0.0132275	-0.0046296
3	2	-1	-0.0223214	0.0211640	-0.0011574
3	2	0	-0.0238095	0.0238095	0.0000000
3	2	1	-0.0223214	0.0211640	-0.0011574
3	2	2	-0.0178571	0.0132275	-0.0046296
3	2	3	-0.0104167	0.0000000	-0.0104167
3	3	-3	-0.0060764	0.0000000	-0.0060764
3	3	-2	-0.0104167	0.0000000	-0.0104167
3	3	-1	-0.0130208	0.0000000	-0.0130208
3	3	0	-0.0138889	0.0000000	-0.0138889
3	3	1	-0.0130208	0.0000000	-0.0130208
3	3	2	-0.0104167	0.0000000	-0.0104167
3	3	3	-0.0060764	0.0000000	-0.0060764
4	0	-4	-0.0090909	0.0000000	-0.0090909

4	0	-3	-0.0161616	0.0138889	-0.0022727
4	0	-2	-0.0212121	0.0238095	0.0025974
4	0	-1	-0.0242424	0.0297619	0.0055195
4	0	0	-0.0252525	0.0317460	0.0064935
4	0	1	-0.0242424	0.0297619	0.0055195
4	0	2	-0.0212121	0.0238095	0.0025974
4	0	3	-0.0161616	0.0138889	-0.0022727
4	0	4	-0.0090909	0.0000000	-0.0090909
4	1	-4	-0.0087273	0.0000000	-0.0087273
4	1	-3	-0.0155152	0.0130208	-0.0024943
4	1	-2	-0.0203636	0.0223214	0.0019578
4	1	-1	-0.0232727	0.0279018	0.0046291
4	1	0	-0.0242424	0.0297619	0.0055195
4	1	1	-0.0232727	0.0279018	0.0046291
4	1	2	-0.0203636	0.0223214	0.0019578
4	1	3	-0.0155152	0.0130208	-0.0024943
4	1	4	-0.0087273	0.0000000	-0.0087273
4	2	-4	-0.0076364	0.0000000	-0.0076364
4	2	-3	-0.0135758	0.0104167	-0.0031591
4	2	-2	-0.0178182	0.0178571	0.0000390
4	2	-1	-0.0203636	0.0223214	0.0019578
4	2	0	-0.0212121	0.0238095	0.0025974
4	2	1	-0.0203636	0.0223214	0.0019578
4	2	2	-0.0178182	0.0178571	0.0000390
4	2	3	-0.0135758	0.0104167	-0.0031591
4	2	4	-0.0076364	0.0000000	-0.0076364
4	3	-4	-0.0058182	0.0000000	-0.0058182
4	3	-3	-0.0103434	0.0060764	-0.0042670
4	3	-2	-0.0135758	0.0104167	-0.0031591
4	3	-1	-0.0155152	0.0130208	-0.0024943
4	3	0	-0.0161616	0.0138889	-0.0022727
4	3	1	-0.0155152	0.0130208	-0.0024943
4	3	2	-0.0135758	0.0104167	-0.0031591
4	3	3	-0.0103434	0.0060764	-0.0042670
4	3	4	-0.0058182	0.0000000	-0.0058182
4	4	-4	-0.0032727	0.0000000	-0.0032727
4	4	-3	-0.0058182	0.0000000	-0.0058182
4	4	-2	-0.0076364	0.0000000	-0.0076364
4	4	-1	-0.0087273	0.0000000	-0.0087273
4	4	0	-0.0090909	0.0000000	-0.0090909
4	4	1	-0.0087273	0.0000000	-0.0087273
4	4	2	-0.0076364	0.0000000	-0.0076364
4	4	3	-0.0058182	0.0000000	-0.0058182
4	4	4	-0.0032727	0.0000000	-0.0032727

When the external electric field is not parallel to electric vector of the microwave field but perpendicular to it, the cases for $\Delta M = \pm 1$ components are observed. The displacements from the rotational line between two states $E^{(1)}_{J+1KM\pm1}$ and $E^{(1)}_{JKM}$ are given by

$$\Delta v = [-\mu E \frac{K(M\pm1)}{(J+1)(J+2)}] - [-\mu E \frac{KM}{J(J+1)}] = \frac{\mu E(2M\mp J)K}{J(J+1)(J+2)}, \tag{21}$$

and the line strengths will be changed to

$$S(JKM \rightarrow J+1KM\pm1) = \begin{pmatrix} J+1 & 1 & J \\ M+1 & -1 & -M \end{pmatrix}^2 \quad \text{or} \quad \begin{pmatrix} J+1 & 1 & -J \\ M-1 & 1 & -M \end{pmatrix}^2 \tag{22}$$

The Stark effect of CD_3F [18] for this case have been investigated previously. The experimental measurements of the rotational lins $1_1 \rightarrow 2_1$ will be discussed below. The magnitudes of the energy elements of Stark effect for both rotational states are given in Table 5. The line strengths calculated by Eq. (22) are listed in Table 6.

Table 5. Stark effect energy elements of rotational states $|11\rangle$ and $|21\rangle$ for CD_3F.

J \ M	-2	-1	0	1	2
1		0.500000	0.0	-0.500000	
2	0.333333	0.166666	0.0	-0.166666	-0.333333

Table 6. Line strengths and energy matrix element differences of Stark effect for rotational states $|11\rangle$ and $|21\rangle$

States / ΔM	J' K' 1 1	J K 2 1	Energy matrix element differencs	Line strength
-1	-1	-2	-0.166666	0.20000
1	-1	0	-0.500000	0.03333
-1	0	-1	0.166666	0.10000
1	0	1	-0.166666	0.10000
-1	1	0	0.500000	0.03333
1	1	2	0.166666	0.20000

From Table 6 we find that there are six components, but two pairs are coincident, so that only four components can be observed. They are ± 0.166666 ($\pm 1/6$) and ± 0.5000 ($\pm \frac{1}{2}$). The line strengths of the coincident pairs will also be added, finally they are 0.3 and 0.03333. Which indicates that these are symmetrically placed about the rotational line with line strengths 1:9:9:1. When the electric field is weak the first-order perturbation is accurate enough. If the electric field is getting stronger, the second-order perturbation shall be taken into account. The second-order corrections for the Stark effect shown above were considered. The first and second-order corrections for both states are respectively given in Tables 7 and 8. The spectral shifts for both orders are shown in Table 9.

Table 7. First-and second-order corrections of Stark effect for $|11\rangle$ of CD_3F, E=1500 v/cm, μ=1.868D.

M	Frist-order (MHz)	Second-order element	Second-order (MHz)	Total (MHz)
-1	705.32	-0.037500	-3.65	701.67
0	0.00	-0.050000	-4.87	-4.87
1	-705.32	-0.037500	-3.65	-708.97

Table 8. First-and second-order corrections of Stark effect for $|21\rangle$ of CD_3F, E=1500v/cm, μ=1.868D.

M	Frist-order (MHz)	Second-order element	Second-order (MHz)	Total (MHz)
-2	470.21	-0.021164	-2.06	468.15
-1	235.11	0.003638	0.35	235.46
0	0.00	0.011905	1.16	1.16
1	-235.11	0.003638	0.35	-234.76
2	-470.21	-0.021164	-2.06	-472.27

Table 9. Line strengths and displacements for first- and second-order perturbation on $1_1 \rightarrow 2_1$ of CD_3F.

States / ΔM	J'K' 1 1	J K 2 1	Frist-order (MHz)	Frist &Second -orders (MHz)	Line Strength
-1	-1	-2	-235.11	-233.52	0.200000
1	-1	0	-705.32	-700.51	0.033333
-1	0	-1	235.11	240.33	0.100000
1	0	1	-235.11	-229.89	0.100000
-1	1	0	705.32	710.13	0.033333
1	1	2	235.11	236.70	0.200000

At stronger field, when the second-order corrections become significant, the coincident pairs due to degeneracies are removed, and six components will be observed as shown in Figure 2.

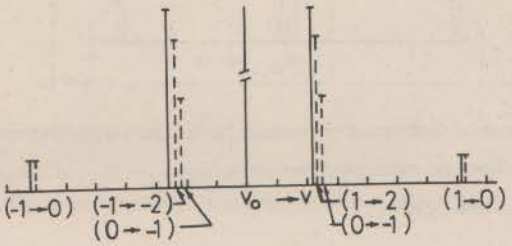

Figure 2. Pattern of line strengths and displacements of Stark effect on rotational transition line $1_1 \rightarrow 2_1$ of CD_3F. E=1500 v/cm, μ=1.868D. Each scale represents 100 MHz. Solid lines represent first-order correction and dash lines for first-and second-order corrections, (Perpendicular case).

If the electric field is parallel to the electric vector, the Stark effect involving the first and second-orders will be simpler than the perpendicular one. We consider the same rotational line $1_1 \rightarrow 2_1$. The magnitudes of energy matrix elements of the first-order pertubation and line strengths are tabulated in Table 10, and the first and second-orders corrections collected from Tables 6 and 7 are shown in Table 11.

Table 10. Line strengths and energy element differences of Stark effect on $1_1 \rightarrow 2_1$ (parallel case).

J'K' 1 1	J K 2 1	Lower state	Upper state	Difference (Us-Ls)	Line strength
-1	-1	0.500000	0.166666	-0.333333	0.100000
0	0	0.0	0.0	0.0	0.133333
1	1	-0.500000	-0.166666	0.333333	0.100000

The line strengths and displacements about the rotational line are illustrated in Figure 3. It is found that the spectrum shifts with second-order correction are toward the increasing frequency.

Table 11. Line strengths and displacements for first and second-orders perturbation on $1_1 \rightarrow 2_1$ of CD_3F (parallel case).

J'K' 1 1	J K 2 1	First-order (MHz)	First and second -order (MHz)	Line strength
-1	-1	-470.21	-466.21	0.100000
0	0	0.00	6.03	0.133333
1	1	470.21	474.21	0.100000

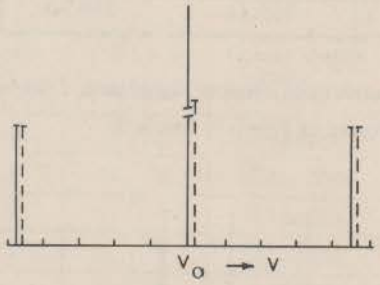

Figure 3. Stark effect pattern of first-order correction (solid line) with first-order and second-order conections (dash line) on rotational transition line $1_1 \rightarrow 2_{10}$ of CD_3F. Each scale represents 100MHz (parallel case).

The Stark effect of HDO [19] on the rotational line $2_{21} \rightarrow 2_{20}$ was measured and the dipole moment was decided to be 0.662D. The line strength used is 3.3030. Strictly speaking, that value is not adequately accurate. Considering the wave functions shown in Table 12 for both states and using the expression for line strength in Ref. 2, we obtain the value 3.315855 for line strength. It yields the dipole moment 0.659D, which is much closer to 0.6567D [20]. The simulated displacements and line strengths on $4_{14} \rightarrow 5_{23}$ of water [21] will be illustrated in Figure 4 and their corresponding magnitudes are listed in Table 13.

Table 12. Wave function and reduced energies of HDO for J = 2, k = -0.6891.

Energy level	Reduced energy	Wave function	Submatrix
2_{20}	2.3499947	-0.0724093| 20> +0.9973750122>	E^+
2_{21}	2.3109000	122>	E^-
2_{11}	-2.7564000	121>	0^-
2_{12}	-3.6891000	121>	0^+
2_{02}	-5.1063946	0.9973750120> +0.0724093 | 22 >	E^+

The line strengths shown in Figure 4 are decreased toward the increasing frequency. The line strengths listed in the last column in Table 2 may also be used for those of asymmetric rotors.

Table 13. Displacement elements and line strengths on $4_{14} \rightarrow 5_{23}$ of water.

M	Displacement	Line strength	Ratio of line strength
0	-13.09	0.0505050	2.78
1	-11.77	0.0484848	2.67
2	- 7.82	0.0424242	2.33
3	- 1.23	0.0323232	1.78
4	7.00	0.0181818	1.00

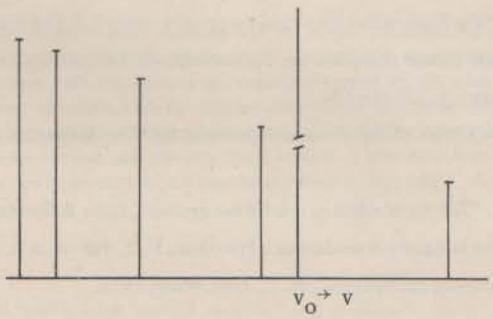

Figure 4. Stark effect pattern on rotational transition line $4_{14} \rightarrow 5_{23}$ of H_2O. The scale of frequency is arbitrary.

IV. Conclusions

The energy levels and line strengths of the Stark effect for both symmetric and asymmetric rotors have been calculated by means of the first-order rotational representations. The explicit forms are in 3j symbols. The fact that the relative intensity of Stark effect includes the line strength of rotational line shows more physical feeling than the previous form does. The second-order perturbation for both kinds of rotors also involves the rotational line strength, so that the accuracy of line strength is important for determining the dipole moment. A little error will affect the deviation of dipole moment. The decision of the dipole moment in HDO mention in Ref. 19 is an example. The Stark effect spectra are used to determine the dipole moment in molecules, and the decided dipole moment comes back for checking consistence. The Stark effect spectra are also used to help identifying very low J rotational transitions which are used to decide the molecular structure. For the spectra of Stark effect, the magnitudes of the rotational energy levels and line strengths have to be calculated. There is no any new procedure calculating the rotational energy levels to replace the traditional one shown in Ref. 15. The reduced Stark coefficients listed in Ref. 8 do not essentially help too much, since the interpolation still has to be used for an proper asymmetry parameter. The individual coefficient of the direction cosine matrix elements tabulated in Ref. 11 might be useful only for $J < 2$. The calculations of spectra of Stark effect for $J > 2$ shall be performed by the starting point of the rotational transition line strength. In conclusion this paper suggests a simple and convenient approach for dealing with the computation of Stark effect, by which the lengthy work can be furtner reduced.

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